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A Study of the Sodium Aluminate-Abietate Size Precipitates

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A STUDY OF THE SODIUM ALUMINATE-ABIETATE SIZE PRECIPITATES

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INTRODUCTION

One of the several outstanding properties required of a sheet of paper or board is the resistance to water penetration. Theoretically, the penetration of water into a sheet of paper can be prevented or retarded by creating and maintaining fiber surfaces which have sufficiently low free surface energies. In practice, the most common way of doing this has been to precipitate rosin size with papermaker's alum, in the presence of the fibers. This process is called internal rosin sizing.

Various sizing problems plague the practical papermaker. Some mills encounter poor sizing during the summer months or when high temperatures are employed. Others encounter extreme variations in the degree of sizing from day to day or even from shift to shift. The problem of "fugitive" sizing afflicts other mills.

In an attempt to solve these problems, investigations have been conducted to elucidate the mechanism of the rosin-alum internal sizing process. These investigations have dealt chiefly with the physical and chemical properties of the size precipitates and the cellulose fiber. Some of these properties are chemical compositions, electrokinetic potentials, and the contact angles which these substances form with water.

Robinson (1) could not correlate the composition of the size precipitate with the degree of sizing it imparted to cellulose fibers. He could not separate the precipitate into any constituents other than

alumina and a chloroform-soluble fraction which had a chemical composition similar to that of the theoretical aluminum triabietate. He did not establish that this chloroform-soluble material was a single compound. When the size was precipitated in the presence of cellulose fibers, Robinson detected free abietic acid. He explained this as a hydrolysis of the triabietate caused by the pulp.

Back and Steenberg (2) studied the composition and properties of aluminum abietates. Abietic acid and its isomers are the chief constituents of rosin. These workers also determined that the contact angles of water on films of aluminum monoabietate or diabietate were 15° higher than those of water on abietic acid.

Back (3) deduced the theoretical relationships between the over-all composition of the solid abietic acid-aluminum diabietate coprecipitate and the activity of abietic acid for possible phase compositions. He showed experimentally that the phase diagram for coprecipitates of various over-all compositions correspond to that which describes two separate phases. Back considered this good evidence that abietic acid and the diabietate exist in the coprecipitate not as a complex but as two separate compounds.

Ekwall and Bruun (4, 5) studied the reaction between the aluminum ion and rosin acid by means of a surface balance. They placed a monolayer of rosin acid over a substrate of aluminum sulfate, then skimmed off the resulting monolayer. The lowest aluminum ion concentration and the lowest pH at which the reaction could be detected were

determined. Likewise, it was possible to define the limiting conditions which caused the reaction to cease. The properties and composition of the monolayer at these limiting conditions were investigated. The analysis indicated that the substance forming the monolayer was composed of dibasic aluminum monorosinates. The term rosinates refers to a mixture of salts of the rosin acids as they occur in rosin. These workers verified the observations of Back and Steenberg that the monorosinates were more water repellent than the free rosin acids.

Price (6) studied the composition of precipitates formed from alum-rosin systems containing varying amounts of free rosin acids. She concluded that the precipitates consisted of dirosinates and free rosin acids. She also concluded that the ratio of free rosin acids to the dirosinates can vary over a large range without affecting the sizing efficiency of the size precipitates.

By means of a potentiometric titration, Price (7) was able to determine the amount of alumina in a size precipitate. She concluded that a "normal" size precipitate contained little or no free alumina. A "normal" precipitate was prepared by adding 25 ml. of 3% size (70% total solids, 20% free rosin) to a liter of distilled water and adding alum to a pH of 4.5. When excess alkali was added to the process water, alumina was detected as a coprecipitate.

Jayme and Seidel (8) claim to have isolated the aluminum trirosinate and have assigned it a melting point of 145-150°C. They formed the precipitate from sodium rosinate and alum at a pH of 4.5. They

found this material to be completely soluble in chloroform, benzene, and methylene chloride. It was stable only in chloroform. An analysis of this solution showed 5.5% Al_2O_3, closely corresponding to the theoretical alumina content of the trirosinate.

In moist solvents, the above size precipitate was unstable, causing Jayme and Seidel to assume that some hydrolysis occurred. A residue with a high alumina content precipitated. This residue was believed to consist of mono- or dirosinates. The supernatant liquor became low in aluminum, indicating the presence of free rosin acid. From these data, Jayme and Seidel concluded that the initial precipitate is composed of trirosinates which hydrolyze to the dirosinates and free rosin acids.

Cobb and Lowe (9) interpreted the alum-rosin sizing mechanism from the viewpoint of coordination chemistry. These investigators found that the presence of oxalate, citrate, and tartrate greatly reduced the sizing efficiency of the alum-rosin system. They concluded that the abietate ions in the size precipitate were partially replaced by the oxalate, citrate, and tartrate ions which have high coordinating tendencies. On the other hand, abietate ions were not appreciably replaced by anions such as sulfate, chloride, or nitrate, which have low coordinating tendencies.

However, Wilson (10) is of the opinion that even these inorganic anions, if present in sufficient concentrations, may inhibit sizing. He believes that sizing at a given high pH is considerably better with a mixture of alum and sodium aluminate than with alum and some alkali, because less sulfate is introduced.

Collins, Davis, and Rowland (11) observed the nature and rate of the precipitation of alumina from alum and aluminum chloride by sodium hydroxide. They also determined the electrophoretic mobilities of alumina particles precipitated at various pH levels. The isoelectric points of alumina from aluminum chloride and alum were found to be at pH values of 9.0 and 7.5, respectively. At higher pH levels, the electrokinetic potential was negative, whereas at lower pH levels, the electrokinetic potential was positive.

Similar electrophoretic mobility determinations were observed for various size precipitates. Saponified rosin and Prosize, a protein stabilized high free rosin size, were separately precipitated by alum, and also by aluminum chloride. The precipitations were carried out at various pH levels and the isoelectric points of all four precipitates were found to be in the pH range of 5.6 to 5.9. If rosin size was precipitated by either sulfuric or hydrochloric acids, the isoelectric points became 4.4 and 4.6, respectively. Thus, the necessity for the presence of the aluminum ion or a similar highly coordinating cation becomes apparent if the size precipitate particles are to be positively charged.

Thode and co-workers (12) have studied the nature of the electrokinetic potential of alum-rosin size precipitates. They have also studied the electrokinetic potentials of sized and unsized cellulose fibers. Ninck Block (13) has also conducted such a study. This work will be discussed more thoroughly in a later section on electrokinetics.

In the early 1940's, it was discovered that a portion of the alum used in sizing could be replaced by sodium aluminate. With the use of sodium aluminate, it has become possible for many mills to increase the pH of sizing to as high a level as 7.0, and still maintain satisfactory sizing (10, 14-17). Several advantages have been demonstrated in these systems as a result of the increased sizing pH. They are better and more permanent sheet strength properties, lowered chemical costs, and reductions in paper machine corrosion.

A review of the literature has failed to reveal any basic studies of the sodium aluminate-rosin or sodium aluminate-abietate sizing system. Therefore, a study of some of the physical and chemical properties of the sodium aluminate-abietate size precipitates was undertaken in this thesis.

PRESENTATION OF THE PROBLEM

The aim of this thesis was to study some of the chemical and physical properties of sodium aluminate-abietate size precipitates in order to help clarify the mechanism of internal rosin sizing of paper and board. A review of the literature indicated that two important variables in the sizing process are the rosin to aluminum ratio and the pH of sizing. The use of sodium aluminate and acid permits separate control of the aluminum and hydronium ion concentrations. Therefore, the sodium aluminate-sodium abietate-acid system was chosen for investigation. With this system, it was possible to separate, for the first time, the effects of the two variables, abietate to aluminum ratio and pH of precipitation, on certain properties of the size precipitates.

The effect of two variables on four important properties of the size precipitate were studied. The two variables were:

1) The initial abietate to aluminum mole ratio in solution prior to precipitation, and
2) The pH of precipitation.

The four properties which were studied were:

1) The composition of the precipitate,
2) The relative free surface energy of the precipitate as reflected by the contact angle which a droplet of water made on a film of the precipitate,
3) The electrokinetic potential of the precipitate particles, and
4) The ability of the precipitate to size wood cellulose fibers.

EXPERIMENTAL PROCEDURES

PREPARATION OF SIZE PRECIPITATES

REACTANTS

The reactants in this study were sodium abietate, sodium aluminate, and perchloric acid. The reaction medium was deionized distilled water.

Sodium abietate was prepared by saponifying pure abietic acid with a 10% excess of 0.3N sodium hydroxide. This saponification was conducted on a steam bath and under nitrogen. The suspension was then diluted with deionized distilled water to an abietate concentration of 5%. This gave a clear, pale straw-colored solution.

Pure abietic acid was prepared by the method of Palkin and Harris (18). Six hundred grams of WW grade rosin were dissolved in 500 ml. of ethanol and boiled with 5 ml. of concentrated hydrochloric acid and one gram of hydroquinone for half an hour. Abietic acid crystallized slowly on cooling. The acid was dried, weighed, and dissolved in benzene, to which was added a stoichiometric amount of n-butyl amine. After two recrystallizations, 125 g. of the salt were obtained as a faintly yellow product. The salt is relatively stable and can be stored. The pure acid was prepared by dispersing the salt in ethyl ether, and adding enough ethereal hydrogen chloride to decompose the salt. The ether-insoluble butylamine hydrochloride was filtered off, and the ether solution was concentrated under a stream of nitrogen. The dried residue of

abietic acid was dissolved in acetone, and recrystallized twice from this solvent. Abietic acid was finally obtained in the form of large colorless crystals, approximately 4 mm. long. Its melting point was 168 to 172°C. and it exhibited an optical rotation of $[\alpha]_D^{23} = -96.5°$ to $-101.0°$ (c-1, absolute ethanol). The acid was vacuum dried and stored under nitrogen.

A stable solution of sodium aluminate was prepared by dissolving a Baker and Adamson mixture of reagent-grade sodium aluminate and sodium hydroxide in water. This mixture was composed of 75% sodium aluminate and 25% sodium hydroxide.

All of the water used in this work was specially purified in order to eliminate the effects of foreign ions. This was accomplished by passing distilled water through an ion-exchange column whose dimensions were 330 by 45 mm. The column was packed with one pound of Amberlite MB-3 mixed resin. When distilled water was passed through this column at the rate of 220 ml. per minute, the effluent exhibited a specific resistance of 1.125 megohm-cm., compared to the specific resistance of 0.175 megohm-cm. for the distilled water.

The pH of the size precipitation system was controlled with a 1% aqueous solution of chemically pure perchloric acid.

PRECIPITATION

The precipitations of the size flocs were carried out in a 4-liter beaker at room temperatures ranging from 20 to 25°C. To the beaker

were added 3 liters of purified water, 6 ml. of 5% sodium abietate solution, and enough sodium aluminate solution to give the desired abietate to aluminum ratio. The alkaline solution was thoroughly mixed by means of an air-driven stirrer. The pH was then slowly lowered by adding 1% perchloric acid from a buret, the stirring being continued throughout the acid addition. The addition of the acid was stopped when the desired pH of the suspension was reached. The pH of the system was constantly monitored by means of a Beckman pH meter, using glass and standard calomel electrodes.

ISOLATION

The size precipitate was isolated by centrifuging the dilute suspension discussed above. The suspension was passed through a Sharples type T-1 steam-driven continuous cylindrical supercentrifuge. This centrifuge develops a bowl speed of 50,000 r.p.m. and a centripetal acceleration of 61,500 G at the cylinder wall. The rate at which the suspension was passed through the centrifuge varied from 75 to 300 ml. per minute, depending upon the particle size of the suspension.

A heavy cellophane liner was placed inside the centrifuge cylinder, and the size precipitate particles were collected on it. At the end of the centrifuging period, the wet precipitate was gently scraped off the liner, and placed in a weighing bottle. The precipitate was dried in a 40°C. vacuum oven in two steps. These steps consisted of drying over magnesium perchlorate for eighteen hours, and then over fresh phosphorous pentoxide for twelve hours or to constant weight within a three-hour period.

The dry precipitate was then ground up into a fine powder, and stored in a small flask under anhydrous nitrogen.

ANALYSIS OF SIZE PRECIPITATES

SEPARATION INTO COMPONENTS

Since it was believed that the isolated size precipitates were actually mixtures of coprecipitated compounds, it was thought desirable to separate the mixtures into their component parts. A simple way of accomplishing this was by selective solvent extractions. It was believed that these mixtures could contain up to three different kinds of compounds. These are abietic acid, aluminum abietates, and aluminum hydroxide. Traces of sodium perchlorate could also be present.

A portion of the dry pulverized size precipitate was extracted with purified acetone to remove the abietic acid. The extract was reserved for analysis, and the residue was dried in a vacuum oven over activated charcoal at 40°C. This residue was weighed and then extracted with a 2:1 mixture of purified chloroform and benzene. The extract, containing aluminum abietates, was concentrated under a stream of nitrogen at room temperature, and the residue from this evaporation was further dried in a vacuum oven at 40°C. over activated charcoal. The dried residue was weighed and stored under nitrogen for further analysis.

The residue from the chloroform-benzene extraction was expected to contain only aluminum hydroxide. This residue was dried in a vacuum oven at 40°C. over activated charcoal, weighed, and reserved for analysis.

All extractions were carried out in 13 by 120-mm. covered test tubes. Approximately 0.5 g. of the size precipitate was extracted with 5 ml. of purified acetone. The same ratio of solids to solvent was used in the chloroform-benzene extraction. After gentle stirring and shaking, the mixture of solids and solvent was centrifuged in a clinical centrifuge at 3500 r.p.m., a speed which developed a centripetal acceleration of 2460 G. The supernatant solution was decanted and reserved, and the residue was washed with 2 ml. of the pure solvent and recentrifuged. The wash liquid was combined with the main extract. The total time of contact between the solids and solvent was 40 minutes.

Earlier attempts to separate the components of size precipitates by solvent extractions were not successful. The reason for this was that aluminum abietates readily undergo hydrolysis, and apparently insufficient care had been taken in purifying the solvents and in maintaining a moisture-free atmosphere during the extractions. It was hoped that hydrolysis could be sufficiently retarded by carefully purifying the solvents and by carrying out all the extractions and manipulations in a box in which the relative humidity was kept below 4%.

The acetone was purified by refluxing 1.5 liters of c.p. acetone with 10 g. of potassium permanganate and 10 g. of potassium carbonate for three hours, then distilling it into a bottle containing potassium carbonate. The chloroform was purified by distilling reagent-grade chloroform twice in the presence of calcium chloride. Thiophene-free benzene was simply distilled twice, and the fraction boiling between 79.8 and 80.1°C. was collected. All of the purified solvents were stored

in ground-glass stoppered bottles and the bottles were kept in a moisture-free cabinet.

ANALYSIS OF COMPONENTS

Abietic Acid

Abietic acid in the size precipitate was determined by a nonaqueous titration described by J. S. Fritz (19). The method was slightly modified for this thesis. Two milliliters of the acetone extract of the isolated size precipitate were dissolved in 18 ml. of 4 to 1 benzene-methanol and placed in a 50-ml. beaker. Two drops of thymol blue indicator solution were added, and the sample-containing solution was titrated with 0.1N sodium methoxide with the aid of a magnetic stirrer. A piece of cardboard with a hole in it to accommodate the buret was placed over the beaker during the titration to minimize the effect of atmospheric carbon dioxide.

The indicator solution was prepared by dissolving 0.3 g. of thymol blue in 100 ml. of methanol. The sodium methoxide solution was prepared by dissolving 5 g. of freshly cut, methanol-washed sodium in 100 ml. of methanol. When the reaction was completed, 150 ml. of methanol and 1500 ml. of benzene were added, and the reagent was stored in a pyrex bottle. The reagent was standardized periodically against benzoic acid.

Abietate

The chloroform-benzene soluble fraction contained aluminum abietates,

and thus had to be analyzed for both aluminum and abietate. The chloroform-benzene insoluble fraction should have contained only aluminum hydroxide, but it, too, was analyzed for abietate.

Since the carbon content of the abietate molecule was known, and since the abietate molecule was the only source of carbon in these fractions, a carbon analysis of these fractions was found to be the simplest and most accurate means of determining the abietate content. These carbon-hydrogen analyses were conducted by the Institute microanalytical laboratory according to the method of Niederl and Niederl (20).

The carbon content of the abietate molecule was determined by analyzing a sample of the original abietic acid prepared for this work. The experimental value of 79.16% carbon agreed closely with the theoretical value of 79.42%.

Aluminum

Both the chloroform-benzene soluble and insoluble fractions were analyzed for aluminum. Determining aluminum gravimetrically by ashing was undesirable for several reasons, the most important of which was that weighing errors become significant when small samples such as those used in this work are used. Consequently, a photometric technique based on the technique described by E. B. Sandell (21) was utilized.

Approximately 10 mg. of the sample were carefully weighed out on

a tared sheet of quantitative low-ash filter paper. The sample was wrapped in this paper and dropped into a 100-ml. Kjeldahl flask, and moistened with water. To it were added 5 ml. of concentrated nitric acid and 2 ml. of concentrated sulfuric acid. This mixture was gently heated until the sample dissolved and the solution turned black from charring. Nitric acid was then added in small portions (a few drops at a time), and the flask was gently reheated until fumes of sulfur trioxide appeared. This step was repeated several times until a colorless liquid was obtained. The flask and contents were allowed to cool, and 2 to 3 ml. of water were added. The flask was heated until white fumes appeared. The solution was cooled, diluted to 50 ml., neutralized with ammonia, and finally diluted to 100 ml.

This solution was then subjected to a photometric aluminum analysis. One to five milliliters of the neutralized solution were transferred to a 100-ml. volumetric flask. Four milliliters of 1.2N hydrochloric acid and 20 ml. of a 10% aqueous ammonium acetate solution were added, followed by 4 ml. of a 0.2% aqueous ammonium aurintricarboxylate solution. The test solution was diluted to volume and the optical density was determined at 520 mmu. The reading was taken exactly 15 minutes after the introduction of the ammonium aurintricarboxylate.

The instrument used to measure the optical density of these solutions was the Bausch and Lomb Spectronic 20 colorimeter, which uses 12 by 100-mm. matched tubes as sample containers. A standard reference curve was determined, using c.p. $Al_2(SO_4)_3 \cdot 18H_2O$ as the standard. The

blanks contained all the reagents but none of the solution to be analyzed. They were used before each determination to properly set the photometer at zero optical density.

MEASUREMENTS OF CONTACT ANGLES OF WATER DROPLETS ON FILMS OF SIZE PRECIPITATES

APPARATUS

The purpose of this instrument was to determine the contact angle between water and a continuous film of the size precipitate. As shown in Figure 1, it was essentially a horizontal microscope through which a photograph of a water droplet resting on a coated glass slide could be taken. The apparatus consisted of the following essential parts (numbers refer to Figure 1):

(1) A 150-watt opaque incandescent lamp,

(2) An infrared filter containing a 2% aqueous solution of copper sulfate,

(3) A 0.6-cm. diaphragm,

(4) A pipet guide,

(5) Brackets which held a 1 by 7-cm. glass microscope slide in a level horizontal position,

(6) A 48-mm. objective lens,

(7) The microscope tube, positioned in the same plane as the glass slide,

(8) A Wetzler 1/2 X adapter which replaces the normal microscope ocular. The front of this adapter fits into the microscope tube and has an eyepiece (9) extending at right angles from

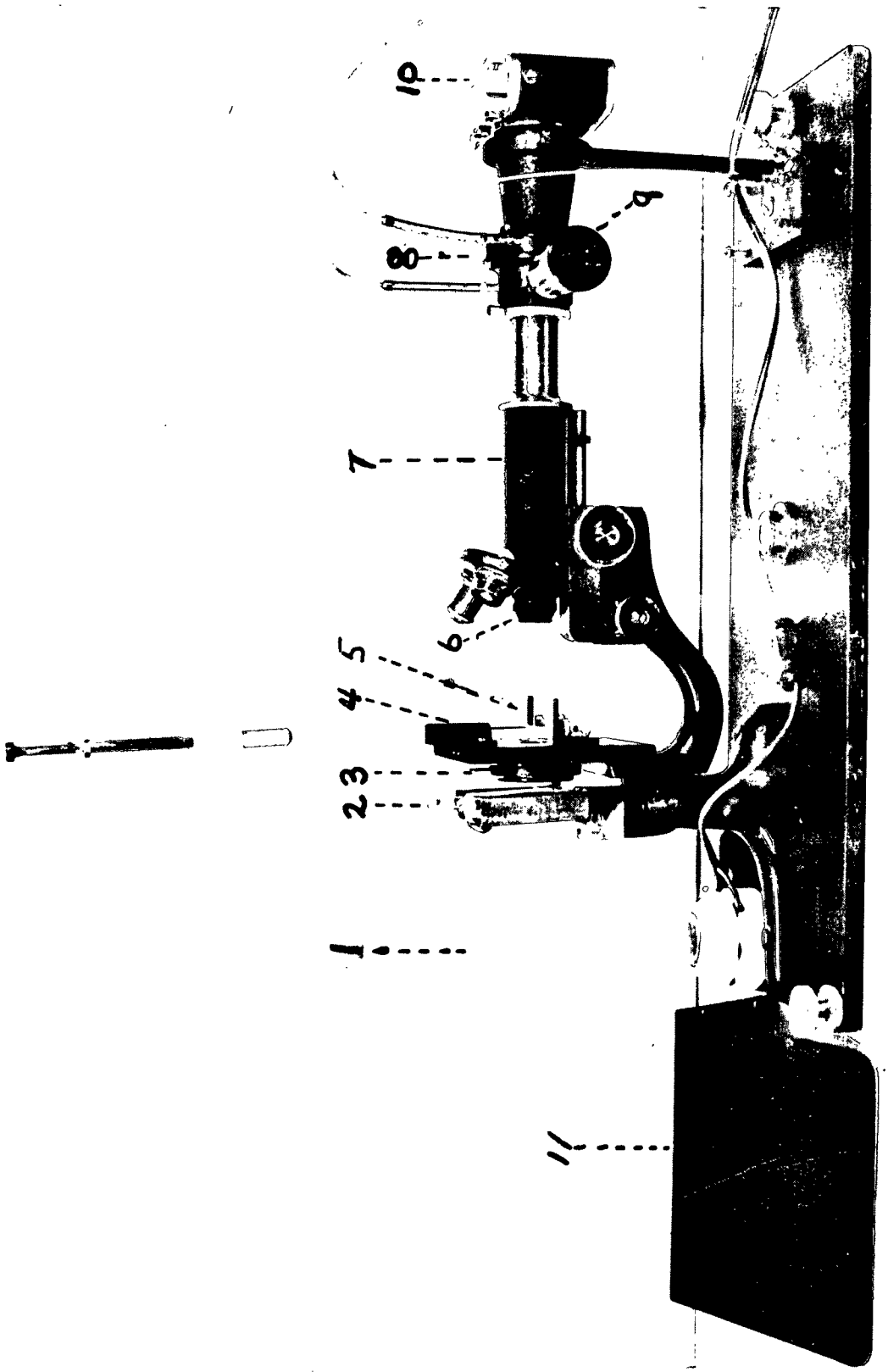

Figure 1

Apparatus For Measurements Of Contact Angles of Water Droplets on Films of Size Precipitates

its main body. One can view the object through this eyepiece by means of a built-in prism. The back of this adapter is threaded to accomodate a 35-mm. Leica camera (10) whose lens system has been removed. The Wetzler adapter contains both the lens and shutter to be used with the camera body. The camera body is used merely as a film holder.

(11) A metal cover for the lamp and filter.

Adox KB 14 black and white film was used throughout this work, and the shutter speed was 1/10 second. There are no adjustable lens openings in the Wetzler adapter. The total magnification obtained with this instrument was 15 diameters.

The instrument was built so that the slide supporting brackets were parallel to the instrument base, and horizontally level. A bubble level and thumb screw legs were installed on the base to make certain that the entire apparatus was properly leveled at all times. Before any measurements were taken, the instrument was prefocused and secured in that position. It was focused on the tip of the pipet, and the leading edge of the glass slide was placed as close to it as possible. In this manner, both the edge of the slide and the outline of the droplet were always in focus.

TECHNIQUE

About 20 mg. of the dried precipitate were dissolved in 2 ml. of purified chloroform. A clean microscope slide which had been split to

a width of 1 cm. was flooded with this solution, and the slide was dried *in vacuo* over activated charcoal. This procedure was repeated four times. Finally, the coated slide was placed over activated charcoal in a 40°C. vacuum oven, and kept there for two hours.

The photographs of the water droplets were taken in a room where the temperature and relative humidity were kept constant at 72°F. and 50%, respectively. The slide was put in place on the brackets, and a clean 3-microliter pipet was filled with purified water by means of a microsyringe. The pipet was placed in its guide and emptied, a small water droplet forming on its tip. This droplet was carefully placed on the slide, and the pipet was lifted. After five seconds of contact between the water and the coated slide, the shutter on the camera attachment was tripped, and the roll of film was advanced one frame. Another picture of the same droplet was taken after 30 seconds of contact. At least two droplets were placed and photographed on each slide.

The developed films were viewed through a photographic enlarger. Since it is difficult to measure contact angles directly, a method which gives a good approximation was employed. This method, used by Back and Steenberg (2) relates the base and altitude of the water droplet to its contact angle with the substrate. If the droplet is assumed to be a part of a sphere, and the effect of gravity is neglected, then,

$$\tan 1/2\ \theta = 2h/b$$

where θ = contact angle measured within the droplet;

h = height of the droplet above the coated glass slide; and

b = the base diameter of the droplet.

This relationship is derived in Appendix I.

MEASUREMENTS OF ELECTROPHORETIC MOBILITIES OF SIZE PRECIPITATE PARTICLES

APPARATUS

The apparatus consisted essentially of a flat microcell through which the particles migrated under an imposed E.M.F., and an ultramicroscope through which this migration was observed. The apparatus and technique were adaptations of those used by Gorham (22). The apparatus is shown in Figure 2, and consisted of the following parts (refer to Figure 2):

(1) Rubber stoppers through which platinum wires, serving as electrodes, were inserted,

(2) Sample reservoirs,

(3) Three-way stopcocks and connecting glass tubing,

(4) A Northrop-Kunitz electrophoresis microcell connected to the glass tubing by small lengths of rubber tubing,

(5) Filar 10X micrometer ocular. This type of ocular has a full view scale and moveable hairline. The distance across the scale was calibrated against a Bausch and Lomb optical grating, and was found to be 448 microns.

(6) The microscope body whose stage was removed,

(7) An 8 mm., 0.5 N.A., 21X objective,

(8) A parabaloid condenser to produce dark field illumination,

(9) An infrared filter of 2% aqueous copper sulfate in a glass container,

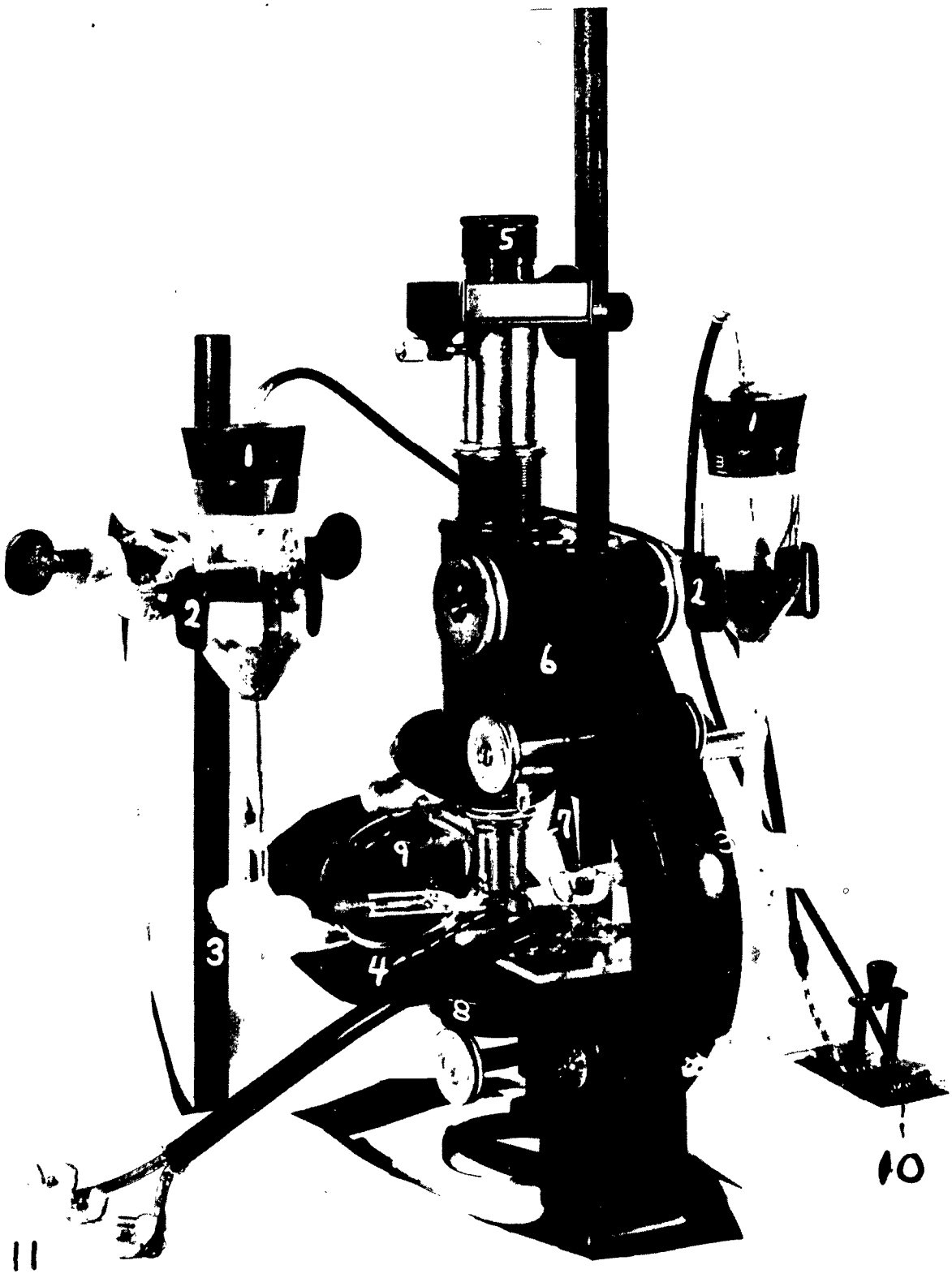

Figure 2

Apparatus For Measurements of Electrophoretic Mobilities of Size Precipitate Particles

(10) A double-throw, double-pole switch to reverse electrode polarity, and

(11) A potential divider leading to a potentiometer.

The light source was a 6-volt, 18-ampere ribbon filament lamp. The light was passed through the filter (9), reflected from the concave side of the sub-stage mirror, passed through the condenser (8), and scattered by the colloidal particles in the electrophoresis cell. When the particles were viewed through the ultramicroscope, they appeared as tiny pin points of light against a dark background.

The electrophoresis cell[a], as shown in Figure 3, was made of two optically flat pieces of glass, whose dimensions were 35 by 14 by 0.8 mm., and which were separated by a gap of 1.039 mm. The edges were sealed together, and to the ends were connected 40-mm. lengths of 6.5-mm. outside diameter, 5.5-mm. inside diameter glass tubing. In these t tubes, and extending into the ends of the flat cell, were attached two platinum probes, which were merely wires of small diameter. The lengths of the wires were coated with glass, so that only the tips made electrical contact with the suspension in the cell. The distance between these tips was measured with a cathetometer and was found to be 3.76 cm.

The function of these probes was to enable one to accurately measure the potential difference existing between them at any given time.

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[a] This cell was built to specifications by Karl Schumann, 681 Jefferson Avenue, Cliffside Park, New Jersey.

The ends of the wires protruding outside the cell were formed in a coil, and connected to copper wires by small nuts and bolts. The copper wires were then connected to a potentiometer circuit. The potential gradient in the cell was calculated by dividing the potential difference existing between the probes by the distance separating them.

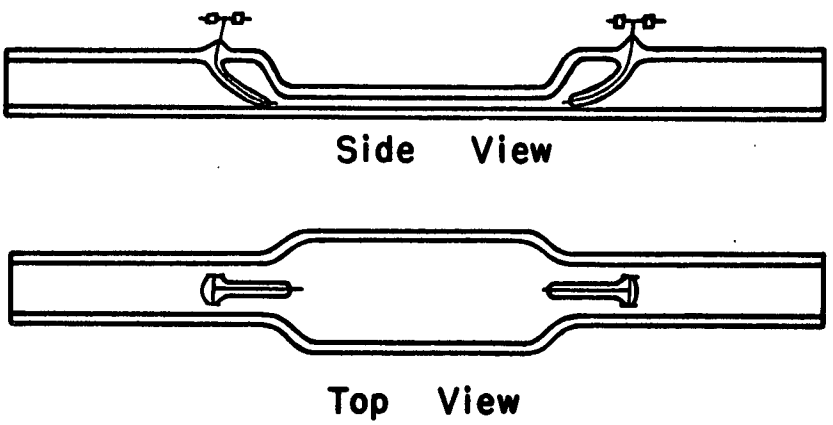


Figure 3. Electrophoresis Cell

The potentiometer chosen for this work was a Cambridge portable model, with a range of 100 millivolts. In order to accommodate the potential difference of up to 100 volts which could be expected in the cell, a potential divider was placed between the cell probes and the potentiometer. The divider consisted of two precision resistors in series. Their resistances were 1 kilohm and 4 megohms, respectively, and they were arranged as shown in Figure 4. The total resistance of this divider had to be high in order to minimize electrolysis at the probes in the cell. A double-throw, double-pole switch was placed between the divider and the potentiometer to allow direct readings when the direction of the current in the cell was changed.

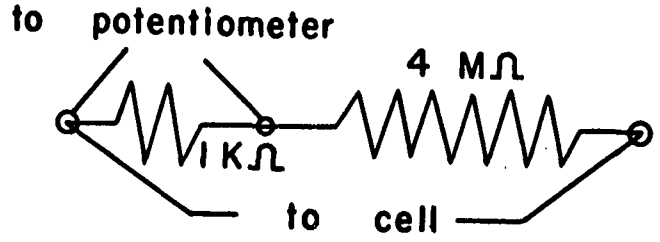


Figure 4. Potential Divider

The platinum electrodes (1) shown in Figure 2 were connected to copper wires which led to a double-throw, double-pole switch, and thence to the power source. This was a Reco model E-800-2 unit, which contains a full-wave rectifier and filtering elements, and is capable of delivering up to 750 volts D.C., and 200 milliamperes. It is line operated on 110 volts A.C.

TECHNIQUE

A suspension of the desired size precipitate was prepared in the manner described on page 11, with the exception that the abietate concentration was lowered to .004%, in order to prevent flocculation. Following Gorham's recommendation, this suspension was subjected to five seconds of high shear stirring in an "Osterizer" blender. This blender treatment produced a stable sol with many particles being visible in the dark field.

Before the start of each run, the cell was flushed out with a large quantity of purified water, alcohol, and again with purified water. Cleaning the cell with sulfuric acid-dichromate cleaning solution was

tried but discontinued, because many hours of tedious rinsing were required to remove the last traces of this solution. If the cell became contaminated or plugged with material which would not rinse out with water or alcohol, nitric acid was used to clean the cell.

After the cell and reservoirs were cleaned and rinsed, the condenser lens was focused. This was accomplished by first removing the tube body from the microscope and turning on the light source. Then by manipulating the adjusting screws on the condenser, and also adjusting the mirror, an image of the diaphragm in the condenser was centered in the lens as the lens was viewed directly from above. At this point, a drop of cedar oil was placed on the condenser lens and the condenser raised until an even film of oil was formed between it and the electrophoresis cell. The tube body was now replaced and the test suspension placed in the reservoirs. Care had to be taken here to free the cell and connections of any trapped air bubbles. The problem of air bubbles was minimized if the cell was kept full of liquid at all times; i.e., the reservoirs were never completely drained when refilling and washing.

The particles adhering to the bottom, inside surface of the cell were brought into focus with the microscope and then, by making fine adjustments on the mirror and condenser, a brilliant dark field illumination was obtained; i.e., a brilliant white glow was shown by all particles against a dark background. This final adjustment was difficult and tedious, so that once it was made, care was taken not to jar the apparatus or change its adjustment. When these precautions were

taken, it was found that no further adjustments were necessary on subsequent runs.

With the dark field condenser lens properly focused, the next step was to focus the objective of the microscope at the proper level in the cell. This level, as shown by Abramson (23) is 21% of the distance between the inside surfaces of the cell. The focus was obtained with the aid of the micrometer head on the fine adjustment screw of the microscope in the following manner. The microscope was focused first on the top inside surface of the cell; then, while counting the number of graduations turned by the micrometer head, the microscope was focused on the bottom inside surface of the cell. Twenty-one per cent of the graduations turned were then computed and the focusing level of the microscope was raised this distance from the bottom of the cell.

When movements of the particles due to gravitational effects could no longer be observed, a potential was applied across the cell. After a few minutes, the particles attained a constant velocity. The potential was slowly adjusted until the time required for one particle to move across the field of view was approximately fifteen seconds. This time was chosen because it was convenient and because it allowed three significant figures to be used in the calculations. The potential across the probes was then read on the potentiometer, and was verified several times during and at the conclusion of each run. The potential gradient in the cell was expressed by the following:

$$\frac{P.R. \times 4 \times 10^{6} \times 10^{-3}}{1 \times 10^{3} \times 3.78} = (1.058 \times P.R.) \text{ volts/cm.,}$$

where P.R. is the potentiometer reading in millivolts.

The direction of the particle migration, and thus the sign of their charge, was first noted. Particles that moved to the left when viewed with the ultramicroscope were actually moving to the right in the cell.

Particles which produced pin points of light when viewed with the ultramicroscope were selected for measurements. Those particles which showed diffraction rings were considered out of focus and therefore at an incorrect level in the cell for electrophoretic measurement. Six suitable particles were picked at random and timed across the scale. The potential was reversed, and six more particles were timed. The time required for a particle to move 448 microns across the ocular scale was measured on a stopwatch.

The electrophoretic mobility was calculated for each direction, and the two values were averaged to yield the true mobility. The electrophoretic mobility is defined as

$$u = \frac{\text{particle migration velocity (microns/sec.)}}{\text{potential gradient in the cell (volts/cm.)}}$$

and is calculated by the following equation:

$$u = \frac{448/\text{sec.}}{1.058 \times P.R.} = \frac{424}{(P.R.)(\text{sec.})} \quad \frac{\text{microns/sec.}}{\text{volts/cm.}}$$

The standard deviation of 30 observations on one sample was determined, and from this it was possible to estimate the precision of this technique. The statistical analysis showed that, within the 95% confidence limits, the error in the average mobilities should not exceed ±7.5%.

DETERMINATION OF SIZING ABILITY OF SIZE PRECIPITATES UPON WOOD CELLULOSE FIBERS

PREPARATION OF PULP

The pulp used in this work was Weyerhaeuser bleached sulfite, made from Western Hemlock. Several sheets of this dry-lapped pulp (485 g.) were torn into 2 by 2-inch squares and placed in a 5-liter Soxhlet extractor. Eight liters of a 2:1 benzene-ethanol mixture were placed in a 12-liter round-bottomed flask and were refluxed on a boiling water bath. The extraction was carried out for 24 hours at a reflux rate of approximately one syphon per hour. The material extracted amounted to 2.06% of the original weight of the pulp.

Most of the air-dried extracted pulp (390 g.) was placed in a 1.5-pound Valley laboratory beater, along with 20 liters of purified water. This mixture was circulated in the beater, without any load on the bedplate, for ten minutes. A load of 5500 g. was put on the bedplate, and the slurry was beaten for 40 minutes to a Schopper-Riegler freeness of 690 cc. The beaten pulp was then dewatered on a table Büchner funnel, shredded in a pulp breaker, and sacked in a polyethylene bag. The moisture content of this pulp was 75.22%. The pulp was stored in a dark room at 40°F.

SIZING OF PULP

A batch of moist pulp (3.76 g. o.d. or 15.20 g. moist) was dispersed in 300 ml. of purified water. The pulp was sized in two different ways. The first was by forming the precipitate before adding the

fibers, and the other was by forming the size in the presence of the fibers. In the first case, preformed precipitates were prepared at the required pH and abietate-to-aluminum mole ratio in the usual manner, but an abietate concentration of 0.005%. The dispersed pulp was then added to the suspension to give a final abietate concentration of 0.004%, and the dilute slurry was slowly agitated with a stirrer for fifteen minutes. The sized pulp slurry was then diluted and the pulp was made into handsheets.

In the second method of sizing, the size was precipitated in the presence of the pulp. In this case, the dispersed pulp was further diluted to the proper sizing consistency, the required amounts of sodium abietate and sodium aluminate were added, and the pH was lowered to the desired level. This slurry was also slowly agitated for fifteen minutes before being further diluted and made into handsheets.

In all cases except those specifically noted, the consistency of sizing was 0.1%, and the concentration of abietate with respect to the fibers was 4.0%.

MAKING AND TESTING OF HANDSHEETS

The slurry of one batch of sized fibers (3.76 liters) contained enough pulp to make two handsheets. The handsheets were made on a rapid Kothen sheet mold at a consistency of 0.04%, without recirculation of the white water. Purified water whose pH had been adjusted with perchloric acid to that of the sizing slurry was used for dilution in the sheet mold.

The sheets were hand couched off the wire with two fresh blotters, and pressed between four blotters for five minutes at 50 p.s.i. They were then dried for seven minutes on a steam-heated drying cylinder whose surface temperature was 105°C. The sheets were then conditioned overnight at 72°F. and 50% relative humidity.

The degree of sizing was determined by the fluorescence size test as recently modified by The Institute of Paper Chemistry (24). The porosity of the sheets was determined by Institute Method 514, using the Gurley densometer.

EXPERIMENTAL RESULTS

COMPOSITION OF SIZE PRECIPITATES

THE CHEMISTRY OF ALUMINUM

Before discussing the chemistry of the sodium aluminate-abietate system, it may be helpful to discuss the chemistry of the aluminum ion. Aluminum is an amphoteric metal, and can therefore exist in a number of combined forms. It is known that the aluminum ion has a coordination number of six in an aqueous solution (25). Therefore, when alum is dissolved in water, the following equilibria may be set up:

$$\left[Al\ (H_2O)_6\right]^{+3} \overset{H_2O}{\rightleftharpoons} \left[Al(OH)(H_2O)_5\right]^{+2} + H_3O^{+1} \qquad (1)$$

$$\left[Al\ (OH)(H_2O)_5\right]^{+2} \overset{H_2O}{\rightleftharpoons} \left[Al(OH)_2(H_2O)_4\right]^{+1} + H_3O^{+1}. \qquad (2)$$

The predominant species is most likely the hexahydrated tripositive aluminum ion. As the pH is raised, however, the basic aluminum ion may appear in greater concentration. As the system is made more alkaline, further hydrolysis occurs and aluminum hydroxide is precipitated. Further addition of alkali will dissolve the hydroxide and yield a basic aluminum ion known as an aluminate.

Sodium aluminate is normally represented as $NaAlO_2$, and when dissolved in water, probably exists in the form $\left[Al(OH)_4(H_2O)_2\right]^{-1}{}_{+Na^{+1}}$ by taking on four molecules of water. This ion can readily hydrolyze to alumina by the following reactions

$$\left[Al(OH)_4(H_2O)_2\right]^{-1} \xrightarrow{H_2O} Al(OH)_3(H_2O)_3 + (OH)^{-1} \qquad (3)$$

Thus, in order to stabilize a sodium aluminate solution, reaction (3) must be repressed by the addition of excess alkali.

It is apparent, then, that aluminum hydroxide can be obtained in two ways. One is by adding acid to a solution in which the aluminum is present as an anion, and the other is by adding alkali to a solution in which the aluminum is present as a cation.

The aluminum ion is an anion exchanger. This property has been aptly described by Pokras (26), who has reviewed the work of A. W. Thomas and others. Thomas and Whitehead (27) prepared alumina sols from aluminum chloride and then treated them with solutions of various salts. The pH of the suspension as a function of the added salt concentration was noted for each salt. Figure 5 reproduces this data.

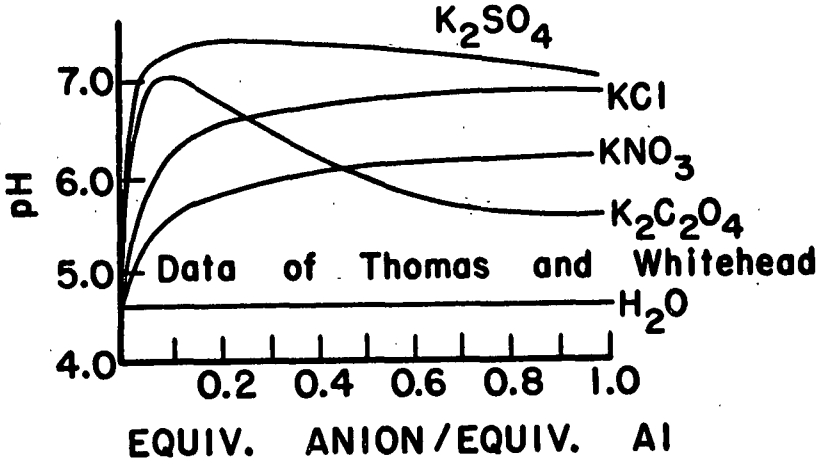


Figure 5. The Effect of Anions on the pH of an Alumina Sol

These data clearly show that the anions are exchanging with the hydroxyls

in the alumina, not merely being adsorbed. Thomas and Whitehead further showed that such anions as tartrate and citrate tend to displace hydroxyl almost completely, and thus prevent the precipitation of any alumina. Weiser (28) found that the composition of a floc precipitated from alum at a pH of 4.5 had a composition very close to $Al_2O_3 \cdot SO_3 \cdot xH_2O$.

Pauley and Testerman (29) titrated lead nitrate with sodium hydroxide and then analyzed the precipitates. At the half-equivalence point, the precipitate composition corresponded to $Pb(NO_3)_2 \cdot Pb(OH)_2$, and at the 5/6 equivalence point, it analyzed $Pb(NO_3)_2 \cdot 5Pb(OH)_2$. Even after adding an appreciable excess of sodium hydroxide, they were unable to obtain pure lead hydroxide. These workers believed that adsorption could not account for this high anion contamination. Instead, they postulated that the lead was acting as an anion exchanger, allowing some hydroxyl ions to be replaced by nitrate ions.

The evidence cited in the preceding paragraphs indicates that hydroxyl ions of hydrous oxides can be replaced by other anions. In a highly alkaline solution, the aluminate ion probably exists in the form $\left[Al(OH)_6\right]^{-3}$ or $\left[Al(OH)_5\right]^{-2}$. At a pH of approximately 10, the aluminate ion probably exists in the form $\left[Al(OH)_4\right]^{-1}$. In a solution of sodium aluminate and sodium abietate, the abietate ion may be expected to exchange with any hydroxyl ion which is combined with the aluminum. These exchange reactions are expressed in Equations 4 and 5.

$$\left[Al(OH)_4\right]^- + Ab^- \rightleftharpoons \left[Al(OH)_3Ab\right]^- + OH^- \qquad (4)$$

$$\left[Al(OH)_3Ab\right]^- + Ab^- \rightleftharpoons \left[Al(OH)_2Ab_2\right]^- + OH^- \quad (5)$$

As the pH is lowered further, several reactions occur.

$$OH^- + H^+ \rightleftharpoons H_2O \quad (6)$$

$$Ab^- + H^+ \rightleftharpoons HAb \quad (7)$$

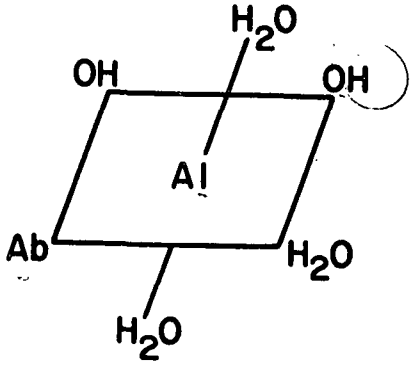
$$\left[Al(OH)_4\right]^- + H^+ \rightleftharpoons Al(OH)_3 + H_2O \quad (8)$$

$$\left[Al(OH)_3Ab\right]^- + H^+ \rightleftharpoons Al(OH)_2Ab + H_2O \quad (9)$$

$$\left[Al(OH)_2Ab_2\right]^- + H^+ \rightleftharpoons Al(OH)Ab_2 + H_2O \quad (10)$$

Assuming that reactions (6-10) are governed by similar equilibrium constants, the ratios of the products will be equal to the ratios of the reactants at any pH of precipitation. From this it follows that the compositions of the isolated size precipitates will be independent of the pH of precipitation, and dependent upon the initial abietate-to-aluminum mole ratio.

Because aluminum has a stable coordination number of six, the products expressed in reactions (8-10) will contain three molecules of coordinately bound water. The probable structure of the aluminum monoabietate molecule is illustrated below.



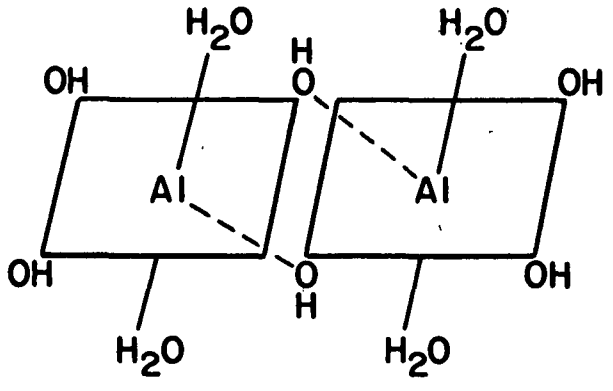
This structure is octahedral, in which all the apices are equivalent.

It is known that when alumina sols are dried or aged, they undergo chemical and physical alterations which are reflected in such properties as solubility in dilute acids and alkalies, x-ray patterns, etc. According to Weiser (30), this gradual change in properties is frequently attributed to a transformation from one allotropic form to another, but more often, it is due to growth and agglomeration of minute particles into larger granules and agglomerates.

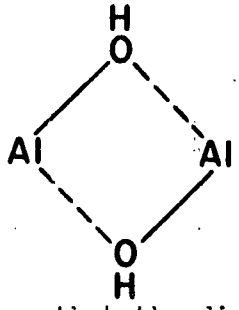
Pfeiffer (31) and later Thomas (32) proposed a mechanism to account for this agglomeration. These workers hypothesized that molecules of hydrous oxides can be bound by so-called hydroxy bridges. This type of bonding was termed "olation," and the specific hydroxyl bridging as "ol" links or bonds. The olation process proceeds in the following manner.

$$Al(OH)_3(H_2O)_3 + Al(OH)_3(H_2O)_3 \rightleftharpoons Al_2(OH)_6(H_2O)_4 + 2H_2O \qquad (11)$$

The probable structure of the olated dimer, according to Thomas, is pictured below.



The dotted lines in Equation (11) represent coordinate linkages, and the segment pictured as

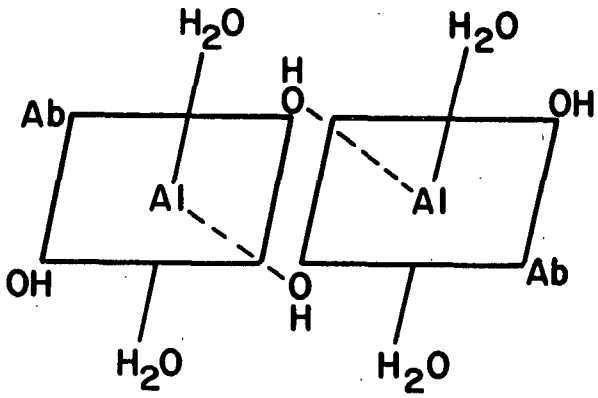


is an ol bond. It can be seen that the dimer in Equation (11) can continue olating with other monomers or dimers. This process can continue until a close network or agglomerate is formed.

In this thesis, the concept of olation was extended to size precipitates by assuming that the aluminum abietates are molecules of partially substituted aluminum hydroxide. The aluminum monoabietates may olate in the following manner.

$$Al(OH)_2Ab(H_2O)_3 + Al(OH)_2Ab(H_2O)_3 \rightleftharpoons Al_2(OH)_4(Ab)_2(H_2O)_4 + 2H_2O \quad (12)$$

The olated product may have the following structure.

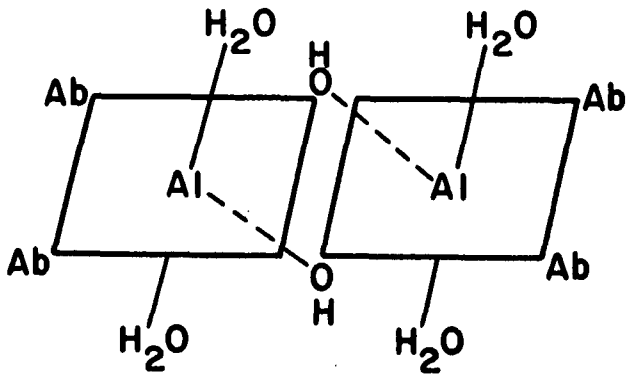


The dimer pictured above will have a lower probability than the aluminum hydroxide dimer for continued olation. The monoabietate dimer now has only four possible positions for further ol bridges.

Aluminum diabietates, at best, can only form dimers, or serve as end blocking groups. They may olate in the following manner.

$$Al(OH)(Ab)_2(H_2O)_3 + Al(OH)(Ab)_2(H_2O)_3 \rightleftharpoons Al(OH)_2(Ab)_4(H_2O)_4 + 2H_2O \quad (13)$$

A possible structure for the dimer is pictured below.



Upon further drying, these olated groups of molecules will lose all of their coordinately bound water. This can be explained by the fact that aluminum is also known to have a stable coordination number of four (33). The chemical composition of such a completely dried olated structure is the same as if it was composed of unassociated anhydrous monomers.

One may visualize how the olation process could proceed in the aging or drying of isolated size precipitates. If the mixture of co-precipitates is rich in aluminum hydroxide, many opportunities would exist for the formation of ol bridges, and many molecules of aluminum abietate would become associated with the aluminum hydroxide. If, on the other hand, the mixture contained very little aluminum hydroxide and mostly abietic acid and aluminum diabietate, very little olation would

occur, and the isolated precipitate would consist largely of monomers and dimers.

The occurrence of olation in size precipitates should affect their solubilities in organic liquids. Hildebrand (34) has studied the solubilities of nonelectrolytes, and has concluded that the solubility of a polymer is directly proportional to the interaction between it and the solvent, and inversely proportional to the polymer's molecular volume. This relationship can be expressed mathematically in the following manner.

$$S = f(\gamma/V) \tag{14}$$

where S = some measure of solubility;

γ = the solute-solvent interaction; and

V = the molecular volume of a polymer molecule.

Since aluminum abietates are soluble in chloroform and benzene, the solute-solvent interaction must be appreciable. Aluminum hydroxide, on the other hand, is insoluble in these solvents, and may be assumed to have a negligible interaction with them. A dimer consisting of one molecule of aluminum monoabietate and one molecule of aluminum hydroxide will exhibit approximately the same solute-solvent interaction as the aluminum monoabietate monomer, since the aluminum hydroxide has contributed very little in this respect. The molecular volume of the dimer, on the other hand, will be significantly greater than that of the monoabietate monomer, being equal to the sum of the individual monomer molecular volumes. Equation (14) predicts that such a dimer will be less

soluble than the aluminum monoabietate in chloroform or benzene. It follows then, that aluminum hydroxide will tend to reduce the chloroform and benzene solubilities of the coprecipitated aluminum abietates by olating with them.

SEPARATION OF SIZE PRECIPITATE COMPONENTS

As stated on page 13 of this thesis, the isolated size precipitates were separated into three components or fractions by means of selective solvent extractions. Table I gives the results of these extractions.

TABLE I

SEPARATION OF SIZE PRECIPITATES INTO COMPONENTS

Initial[a] [Ab]/[Al]	pH of[b] Pptn.	Acetone Soluble, %	Acetone-Insol. Frac. Sol. In 2:1 Chloroform-Benzene, %
2.0	7.5	21.6	100.0
	7.0	23.7	100.0
	6.5	22.4	100.0
	6.0	22.2	100.0
	5.5	24.2	100.0
1.0	7.5	10.9	100.0
	6.5	11.5	100.0
	5.5	13.5	100.0
0.5	7.5	7.9	42.5
	6.5	9.4	41.4
	5.5	8.6	41.0
0.2	7.5	0.4	0.5
	6.5	0.0	1.6
	5.5	0.5	1.2

[a] This is the mole ratio of abietate to aluminum ions existing in the alkaline solution prior to acidification and precipitation.

[b] pH of precipitation.

Both Back and Steenberg (2) and Jayme and Seidel (35) have extracted size precipitates with acetone in an attempt to separate abietic acid from the rest of the alum-abietate precipitate. Jayme and Seidel analyzed the acetone solution for aluminum and found up to 1.2% aluminum in the extract.

As a preliminary part of this thesis, aluminum contents of several acetone extracts were determined and the results are shown in Table II.

TABLE II

ALUMINUM CONTENTS OF THE ACETONE EXTRACTS

Initial [Ab]/[Al]	pH of Pptn.	Extraction Time, hrs.	Al in Extract, %
1.0	6.5	0.7	0.12
2.0	6.5	0.7	0.43
2.0	6.5	39.0	0.30
3.0	5.5	0.7	0.17
4.0	5.5	24.0	0.20

In the case of the size precipitates which had an initial abietate-to-aluminum mole ratio of 2.0 or higher, it was impossible to completely clarify the acetone solution. This was in accord with the observations of Jayme and Seidel (35). This turbidity probably accounted for a part of the aluminum found in the acetone extracts. The maximum possible contamination of the acetone extract with aluminum abietates or aluminum hydroxide was calculated to be less than 5%.

Table III shows the effect of extraction time on the amount of abietic acid extracted.

TABLE III

EFFECT OF TIME ON ACETONE EXTRACTIONS

Initial [Ab]/[Al]	pH of Pptn.	Extraction Time, hrs.	HAb in[a] Size Ppt. %
1.0	6.5	0.7	13.7
1.0	6.5	18.0	11.9
2.0	6.5	0.7	23.6
2.0	6.5	18.0	22.5
2.0	6.5	39.0	25.3

[a] HAb refers to abietic acid in the isolated size precipitate as determined by the sodium methoxide titration on the acetone extract.

These data show that it is unnecessary to extract for more than 40 minutes. Handling and centrifuging made 40 minutes a practical minimum extraction time.

The observations of Back and Steenberg (2) and Jayme and Seidel (35) that aluminum abietates are completely soluble in either anhydrous chloroform or benzene were confirmed. The chloroform solution is more stable, but has the disadvantage of having a high density. This creates a difficulty in separating the extract from the residue by centrifuging. By extracting the acetone-insoluble fraction of the size precipitate with a 2:1 mixture of chloroform and benzene, it was possible to separate the clear supernatant extract and the residue by centrifuging.

ANALYSIS OF SIZE PRECIPITATE COMPONENTS

The abietic acid contents of the isolated size precipitates were determined by sodium methoxide titrations of the acetone extracts. The results are shown in Table IV.

TABLE IV

ABIETIC ACID CONTENTS OF
ISOLATED SIZE PRECIPITATES

Initial [HAb]/[Al]	pH of Pptn.	HAb in Size Ppt., %
2.0	7.5	22.3
	7.0	21.9
	6.5	22.5
	6.0	20.2
	5.5	23.1
1.0	7.5	10.6
	6.5	11.9
	5.5	13.7
0.5	7.5	8.0
	6.5	9.0
	5.5	8.1
0.2	7.5	0.2
	6.5	0.2
	5.5	0.2

Comparison of Table I and Table IV shows that virtually all of the acetone-extractable fraction of the isolated size precipitate was composed of abietic acid.

The chloroform-benzene soluble and insoluble fractions were both analyzed for aluminum, carbon, and hydrogen. This material had been extracted with acetone prior to being extracted with chloroform-benzene. The results of these analyses are shown in Table V.

From the data presented in Table I and Table V, it was possible

to calculate the molar compositions of the isolated size precipitates. These compositions are tabulated in Table VI.

TABLE V

ANALYSES OF ACETONE-EXTRACTED PRECIPITATES

Initial [Ab]/[Al]	pH of Pptn.	Chloroform-Benzene Soluble Fraction			Chloroform-Benzene Insoluble Fraction		
		Al, %	C, %	H, %	Al, %	C, %	H, %
2.0	7.5	5.41	65.83	8.32	—	—	—
	7.0	5.28	67.69	8.51	—	—	—
	6.5	5.47	66.69	8.56	—	—	—
	6.0	5.30	69.79	9.01	—	—	—
	5.5	5.44	65.73	8.53	—	—	—
1.0	7.5	8.47	61.98	8.40	—	—	—
	6.5	8.27	62.40	8.53	—	—	—
	5.5	8.47	60.35	8.32	—	—	—
0.5	7.5	10.10	59.92	8.11	17.20	41.16	6.86
	6.5	10.00	59.68	8.09	17.10	41.34	6.78
	5.5	10.00	59.84	8.13	16.31	40.73	6.72
0.2	7.5	—	—	—	20.50	35.86	6.13
	6.5	—	—	—	20.90	35.13	6.15
	5.5	—	—	—	20.10	35.42	6.10

Inspection of Table VI does not indicate the presence of any stoichiometric compound. On the contrary, it indicates that the size precipitate is actually a heterogeneous coprecipitate of abietic acid, aluminum abietates, and aluminum hydroxide. Further evidence indicating the heterogeneous nature of these size precipitates is shown in Table VII. All of the precipitates began to darken at 280°C. and appeared to decompose upon melting. Precipitates containing abietic acid began to darken at temperatures as low as 250°C.

TABLE VI

MOLAR COMPOSITIONS OF TOTAL PRECIPITATES

Initial [Ab]/[Al]	pH of Pptn.	HAb	Al	Ab	OH[a]	(Ab+HAb)/Al
2.0	7.5	0.51	1.00	1.37	1.63	1.88
	7.0	0.47	1.00	1.44	1.56	1.91
	6.5	0.47	1.00	1.37	1.63	1.84
	6.0	0.43	1.00	1.48	1.52	1.91
	5.5	0.50	1.00	1.35	1.65	1.85
1.0	7.5	0.13	1.00	0.81	2.19	0.94
	6.5	0.15	1.00	0.85	2.15	1.00
	5.5	0.17	1.00	0.80	2.20	0.97
0.5	7.5	0.056	1.00	0.39	2.61	0.45
	6.5	0.057	1.00	0.39	2.61	0.45
	5.5	0.057	1.00	0.40	2.60	0.46
0.2	7.5	0.003	1.00	0.20	2.80	0.20
	6.5	0.003	1.00	0.19	2.81	0.19
	5.5	0.003	1.00	0.20	2.80	0.20

[a] Moles OH obtained by assuming OH=3-Ab in the acetone-insoluble fraction. This is justified by the fact that aluminum is a trivalent cation and abietate and hydroxyl are the only anions in this system capable of associating with it.

TABLE VII

THE EFFECT OF COMPOSITION ON THE SINTERING AND MELTING RANGES OF SIZE PRECIPITATES

Initial [Ab]/[Al]	HAb, %	Sintering Range[b], °C.	Melting Range, °C.
1.0	11.9	200-210	348-360
1.0[a]	0.0	340-350	350-360
2.0	22.5	150-160	352-360
2.0[a]	0.0	330-340	340-355
4.0	63.0	110-125	300-310

[a] These precipitates have been acetone extracted, and presumably contain no free abietic acid.

[b] The sintering range is that range in which small fissures appear in the mass of sample powder, and in which the mass tends to shrink a little.

The sintering range is presumably the range in which the abietic acid melts. Its normal melting point is 168-170°C. The existence of these two widely different melting ranges in unextracted size precipitates is evidence that these precipitates may be composed of at least two different compounds. The fact that the sintering range was almost eliminated if the precipitate was previously acetone extracted indicates that the acetone extraction had removed the material causing the sintering. This is further evidence that the abietic acid existed in the original size precipitates and was not hydrolytically formed during the acetone extraction.

DISCUSSION

The following important observations were made with respect to the preceding data.

1. The compositions of the size precipitates were independent of the pH of precipitation;
2. No precipitate consisting of a stoichiometric compound was isolated; and
3. Some of the isolated precipitates exhibited abnormally low chloroform-benzene solubilities.

The initial abietate-to-aluminum mole ratio is an important factor in determining the composition of the size precipitate, whereas the pH of precipitation appears to have little effect. This result was predicted under the condition that the equilibrium constants governing Equations (6-10) are similar.

Both Back and Steenberg (2) and Jayme and Seidel (35) have studied the effect of pH of precipitation on the alum-abietate system. This system differs from the aluminate system in that the abietate-to-aluminum ratio and the pH are both lowered as more alum is added to a sodium abietate solution. Because of this, it may appear that the composition varies with the pH of precipitation, but it is actually the abietate-to-aluminum mole ratio which is controlling the composition. Back and Steenberg (2) found the composition of their precipitates to be independent of pH. In other words, when they added various amounts of alum to dilute sodium abietate solutions of the same concentration, the over-all compositions of the resulting precipitates remained constant. Jayme and Seidel (35), on the other hand, found that the compositions were highly dependent upon the amount of alum added. Their results, which agree with the theory and experimental observations developed in this thesis, are reproduced in Table VIII. The variable compositions were due to variable initial abietate-to-aluminum mole ratios, and not to variable pH levels of precipitation.

TABLE VIII

ACETONE SOLUBILITY OF SIZE PRECIPITATES FORMED AT VARIOUS pH LEVELS FROM SODIUM ABIETATE AND ALUM (35)

pH of Pptn.	Acetone Soluble, %
4.5	33.75
5.4	35.30
6.2	60.10
7.3	67.70

The experimental results verify the hypothesis (see p. 34 par. 2) that the composition of the isolated size precipitate is independent of pH of precipitation and is dependent upon the initial abietate-to-aluminum mole ratio.

As indicated in Table VI, no single stoichiometric compound was isolated. Although Jayme and Seidel (35) and Robinson (1) concluded that stoichiometric amounts of alum and sodium abietate formed the triabietate, the experimental results of this thesis do not verify the existence of the triabietate.

If a size precipitate is composed of unassociated aluminum abietates and aluminum hydroxide, chloroform-benzene should remove the aluminum abietates from the aluminum hydroxide. Thus, theoretically, the chloroform-benzene solubility of any isolated size precipitate is governed by the percentage of aluminum abietates in the coprecipitate. Table IX shows the theoretical and actual solubilities of acetone-extracted precipitates.

The wide divergence between the theoretical and experimental solubilities could have been due to either a mechanical entrapment of the aluminum abietates by the aluminum hydroxide, or a chemical union between the aluminum abietates and aluminum hydroxide.

The possibility of mechanical entrapment was approached in two ways. It was thought that time of extraction and particle size of the material to be extracted should markedly influence the amount of material extracted. Therefore, two samples of similar particle size

TABLE IX

CHLOROFORM-BENZENE SOLUBILITIES OF ACETONE-EXTRACTED SIZE PRECIPITATES

Initial [Ab]/[Al]	[Ab]/[Al] In Acetone-Extracted Ppt.	Theoretically[a] Soluble, %	Actually[b] Soluble, %
0.50	0.39	64.1	42.0
0.20	0.20	47.9	1.0

[a] These values were obtained by assuming that all of the abietate must be combined as the aluminum diabietate to yield the lowest solubility. Thus, if the [Ab]/[Al] in the acetone-extracted precipitate is 0.4, 0.4 moles of abietate are present with every mole of aluminum. The abietate is combined with 0.2 moles of aluminum, to give 0.2 moles of aluminum diabietate, leaving 0.8 moles of aluminum to be combined as the hydroxide. By converting the mole ratios of these two compounds to weight ratios, and by assuming that only the aluminum diabietate was soluble, the minimum theoretical solubility was calculated.

[b] Values obtained from Table I.

were extracted for 40 minutes and eight hours, respectively. The 40-minute extraction dissolved 41.3% of the total solids, while the eight-hour extraction yielded 41.8%. Another sample of the same material was carefully ground into a very fine powder in a small mortar and pestle. This material was divided into two portions which were extracted for 40 minutes and eight hours, respectively. The amount extracted in these cases amounted to 42.5 and 42.9% of the original solids.

Presumably, therefore, little or no mechanical entrapment of the aluminum abietates existed. It can therefore be deduced that the only

way the normally soluble aluminum abietates were restrained from dissolving was by olating with the insoluble aluminum hydroxide. The effect of olation on solubility was discussed on page 38, where it was postulated that olation between aluminum abietates and aluminum hydroxide would lower the solubility of the aluminum abietates in chloroform and benzene.

From a statistical viewpoint, one would expect this olated structure to consist of polymers in which the mole ratios of aluminum hydroxide to aluminum abietate monomer units would vary over a wide range. Those polymers consisting mostly of aluminum abietates would be soluble in chloroform-benzene. These soluble polymers would contain not only aluminum abietates, but also some aluminum hydroxide.

Of the abietates, the monoabietate contains the most aluminum, 7.45%, whereas the diabietate contains 4.19% aluminum. Table X shows the aluminum contents of the chloroform-benzene soluble, acetone-insoluble fraction of various size precipitates. The chloroform-benzene

TABLE X

ALUMINUM CONTENTS OF THE CHLOROFORM-BENZENE SOLUBLE, ACETONE-INSOLUBLE FRACTION OF ISOLATED SIZE PRECIPITATES

Initial [Ab]/[Al]	Al, %
2.0	5.4
1.0	8.4
0.5	10.0

soluble fractions of those precipitates formed at initial abietate-to-aluminum mole ratios of 1.0 and 0.5 all contained more than 7.45% aluminum

hydroxide in addition to the aluminum abietates. These results are further evidence of the occurrence of olation in some of the size precipitates.

An x-ray diffraction spectrum of a sample of the size precipitate powder with an abietate-to-aluminum mole ratio of 0.2 was determined. The range of x-ray incident angles covered in the spectrum was such as to detect interplaner distances of 0.94 to 22.09 Angstroms. No peaks were observed on the spectrum, indicating a lack of crystallinity in the sample.

Although absolute proof is lacking, evidence based on solubility phenomena strongly indicates that the size precipitates undergo olation during drying. As predicted in the theoretical development of this section, the extent of olation was governed by the aluminum content of the size precipitate.

CONTACT ANGLES OF WATER DROPLETS ON FILMS OF SIZE PRECIPITATES

THE THEORY OF WETTING AND PENETRATION

The purpose of any sizing material is to prevent or retard the penetration of liquids into a sheet of paper or board. If one analyzes the mechanism of penetration, he must utilize the tools and concepts of surface chemistry. It is, therefore, appropriate, at this time, to review the thermodynamic theory of wetting and penetration, and to see how it may be applied to the penetration of water through paper or board. An

excellent review of this theory has been outlined by Schulman and Zisman (36) and the following treatment has been gleaned largely from their paper.

The wetting behavior of solid-liquid systems is best described in terms of the changes in free surface energy of the solid and the liquid. The work of adhesion ($\underline{W}_{SL}$), between the liquid and the solid may be related to the free surface energies per unit area of the solid and liquid in the system by the Dupré equation.

$$\underline{W}_{SL} = \gamma_{S}^{o} + \gamma_{LV}^{o} - \gamma_{SL} \qquad (15)$$

where

γ_{S}^{o} = specific free surface energy of the solid in vacuum;

γ_{LV}^{o} = specific free surface energy of the liquid in equilibrium with its saturated vapor; and

γ_{SL} = specific free surface energy of the solid-liquid interface.

At present no trustworthy method exists for measuring γ_{S}^{o}, so that $\underline{W}_{SL}$ cannot be determined directly. An indirect method of determining $\underline{W}_{SL}$ is available, however.

Young (37) first described the free surface energy equilibrium which exists when a drop of liquid is in contact with a smooth solid surface. His equation is

$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA} \cos\theta \qquad (16)$$

where θ is the contact angle and γ_{SA}, γ_{SL}, and γ_{LA} are the free surface energies per square centimeter of the solid-air, solid-liquid, and liquid-air interfaces, respectively. The latter is mathematically equivalent to the surface tension of the liquid.

Bangham and Razouk (38) showed that the free surface energy per unit area of a clean solid surface will be decreased by the adsorption of the vapor of the liquid. Consequently, they modified the Young equation to read:

$$\gamma_{SV}^{o} = \gamma_{SL} + \gamma_{LV}^{o}\cos\theta_E \qquad (17)$$

or

$$\cos\theta_E = (\gamma_{SV}^{o} - \gamma_{SL})/\gamma_{LV}^{o}$$

where θ_E represents the contact angle when solid, liquid, and vapor are in equilibrium, and the other symbols have the significances defined earlier.

Combining equations (15) and (17) and defining $(\gamma_S^{o} - \gamma_{SV}^{o})$ as $\underline{f}_{SV}^{o}$, they obtained.

$$W_{SL} = \underline{f}_{SV}^{o} + \gamma_{LV}^{o}\,(1 + \cos\theta_E) \qquad (18)$$

Unfortunately, $\underline{f}_{SV}^{o}$ is not simply determined experimentally. Bangham (39) has shown that this quantity, the free energy decrease on immersion of the solid in the saturated vapor, can be calculated from the adsorption isotherm of the solid-vapor system at 20°C. by integrating Gibb's adsorption equation from zero pressure to the saturation pressure of the vapor. Thus,

$$\underline{f}_{SV}^{o} = R\underline{T}\int_{0}^{\underline{P}_o} \Gamma \, d\ln \underline{p} \qquad (19)$$

where

R = the gas constant;

$\underline{T}$ = the absolute temperature;

$\underline{P}_o$ = the saturation pressure in dynes per square centimeter; and

Γ = the surface concentration of the adsorbed molecules in moles per square centimeter.

In the case of volatile liquids, this correction could be quite significant. However, for water at 20°C., the saturated pressure is so low that the correction becomes negligible, unless the adsorbents are hygroscopic. Equation (18) then simplifies to

$$\underline{W}_{SL} = \gamma_{LV}^{o} (1 + \cos\theta_E) \qquad (20)$$

The work necessary to separate a unit area of liquid from itself, i.e., the work of cohesion $\underline{W}_c$ may be expressed as

$$\underline{W}_c = 2 \gamma_{LV}^{o} \qquad (21)$$

which is equal to twice the surface tension of the liquid. If $\underline{W}_c$ is equal to or less than $\underline{W}_{SL}$, the liquid is attracted to the solid more than to itself, and it will spontaneously spread over the solid surface. Consequently, $\cos\theta_E$ will be unity or greater and θ_E will be zero. If $\underline{W}_c$ is greater than $\underline{W}_{SL}$, i.e., the liquid molecules are attracted to themselves more strongly than to the solid, $\cos\theta_E$ must be less than unity, and θ_E will be finite. As $\underline{W}_{SL}$ approaches zero for constant values of $\underline{W}_c$, the contact angle will approach 180°. It is known that all molecules have some attraction for each other, so that $\underline{W}_{SL}$ can never be zero, and θ_E can never be 180°.

The penetration of liquids into porous media such as sheets of paper or board involves the penetration of liquids through capillaries. Although the actual analysis is very complex because of the irregular shapes and sizes of the capillaries, the principle involved here can be explained by the theory of capillarity.

If a liquid surface is curved, the pressure is greater on the concave side than on the convex, by an amount which depends upon the surface tension and on the curvature of the liquid (40). This relationship is expressed mathematically by the following equation:

$$\Delta P = \gamma_{LV}^{o} \left(1/r_1 + 1/r_2\right) \tag{22}$$

where

γ_{LV}^{o} = the specific free surface energy of the liquid, which is mathematically equivalent to the surface tension of the liquid; and

r_1 and r_2 = the principle radii of the curved surface under consideration.

If the curved surface is a part of a sphere, as would be the case if it existed in a uniform circular capillary of radius r,

$$\Delta P = (2\gamma_{LV}^{o} \cos\theta_E)/r \tag{23}$$

If a capillary is extended into a pool of liquid, the liquid will rise in the capillary to a level either above, even with, or below that of the outside pool. The height to which it will rise will depend upon the pressure difference existing in the liquid meniscus in the capillary. If the contact angle between the capillary wall and the liquid is less than 90°, the meniscus will be concave upwards, and according to the theory of capillarity, the liquid will rise above the level of the pool until its gravity head balances the pressure difference across the meniscus.

Likewise, if the contact angle is greater than 90°, the liquid will rise to a level below that of the outside pool. In the first case, the free surface energies of the liquid and solid aided gravity in penetrating the capillary, whereas in the second case, they resisted the penetration.

The rate of penetration of liquids through a capillary may be expressed by the so-called Washburn equation (41). This equation combines Equation (23) with Poiseuille's equation for laminar flow. It reads

$$dL/dT = (\gamma_{LV}{}^{o}\ r\ \cos\theta_E)/4\eta L \qquad (24)$$

where

L = the length of the capillary filled with liquid or the depth of penetration;

r = the radius of the capillary

$\gamma_{LV}{}^{o}$ = the specific free surface energy (surface tension) of the liquid; and

where

η = the viscosity of the liquid;

T = the time of penetration; and

θ_E = the contact angle.

Thus, it can be seen that if the liquid and the geometry of the capillaries are kept constant, the rate of penetration becomes a function of the contact angle, or more fundamentally, a function of the free surface energy of the capillary walls.

THE EFFECT OF SURFACE ROUGHNESS AND POROSITY ON WETTING AND PENETRATION

Two features of paper and board which complicate the simple treatment discussed above are their surface roughness and porosity. The reader is referred to Wenzel (42), Bartell and Shepard (43, 44, 45) and Back and Lundin (46) for thorough discussions of the roughness problem.

The effect of roughness may be understood if one realizes that Young's Equation (17) refers to plane geometrical unit areas. Liquids will conform to this, but few solids will. In other words, the free surface energy change of a rough solid immersed in a liquid will differ from that of a unit plane geometrical surface. This difference will depend upon the ratio, A_1, of actual surface area to plane surface area. The free energy change in forming a liquid-solid interface will then be $A_1(\gamma_{SV}^o - \gamma_{SL})$, and Equation (17) will be modified to read

$$\cos\theta_{AA} = A_1(\gamma_{SV}^o - \gamma_{SL})/\gamma_{LV}^o = A_1\cos\theta_E \qquad (25)$$

where θ_{AA} is the apparent advancing contact angle. In words, then, the effect of roughness is to increase the apparent advancing contact angle when the actual advancing contact angle is obtuse, and to decrease the apparent advancing contact angle when the actual advancing contact angle is acute.

Cassie and Baxter (47) have shown both theoretically and experimentally that when water is placed upon a carefully constructed grid of paraffin-coated wires, the apparent contact angle can be much greater than the actual contact angle. These workers showed that when the distance between parallel wires of a coated grid was twice the diameter of the wires, the apparent contact angle was 143°, although the actual contact angle was only 105°. They point out the fact that a duck gains its excellent water repellency by virtue of the structure and spacing of its feathers, and not because of some superlative sizing agent.

This may best be understood if free surface energy changes are again considered. Let A_1 be the total area of the solid-liquid interface and A_2 be the total area of the liquid-air interface in a plane of geometrical area of unity parallel to the rough and porous surface. The net energy change in covering this unit plane area of rough and porous surface with the liquid can be expressed as

$$\underline{E}_D = A_1(\gamma_{LS} - \gamma_{SV}^o) + A_2\gamma_{LV}^o \qquad (26)$$

Combining Young's Equation (17) with Equation (26)

$$\underline{E}_D = \gamma_{LV}^o(A_2 - A_1\cos\theta_E) \qquad (27)$$

Equation (17) may also be written

$$\cos\theta_E = -\underline{E}/\gamma_{LV}^o \qquad (28)$$

where $\underline{E}$ is the energy required to form a unit area of the solid-liquid interface. An apparent advancing contact angle for a rough and porous surface may then be defined by

$$\cos\theta_D = -\underline{E}_D/\gamma_{LV}^o = A_1\cos\theta_E - A_2 \qquad (29)$$

Equation (29) shows that whereas surface roughness can either increase or decrease the apparent advancing contact angle, the porosity of a surface will always increase the contact angle.

In spite of the fact that one cannot analyze the penetration of water into paper and board very simply, the fact still remains that the most important single factor governing penetration is the free surface energy of the fiber surface. It is this property which determines the actual contact angle.

FACTORS AFFECTING THE CONTACT ANGLE

Unfortunately, the measurement of contact angles is not an easy task, and more often than not, the actual angles observed do not accurately describe the thermodynamic quantities discussed earlier. It must be emphasized that the equations cited in the early part of this section are completely valid only when true equilibrium exists. It is known that the aluminum abietates will undergo hydrolysis as soon as the water droplet touches their surface. Furthermore, surface oxidation is continually changing the chemical structure of the surface.

Most attempts to measure contact angles yield values which may vary between two rather wide limits. One is the receding value, and the other is the advancing value. This existence of a range of contact angles has been termed hysteresis. According to Weiser (48) there are many factors which may influence hysteresis, such as roughness of the surface, the presence of adsorbed films of foreign substances which are removed by the advancing fluid, and the formation of an adsorbed layer from the liquid or liquids used.

The effect of roughness has already been discussed on page 55 of this thesis.

If the solid surface is covered by a film of grease, vapor, or gas, its free surface energy may be lower than that of the pure solid. Thus, when a liquid boundary advances over the surface, it yields an abnormally high angle. However, if this film can be dissolved into the liquid droplet, the receding angle will be lower than the advancing angle.

If the liquid can form an adsorbed layer on the solid surface, the free surface energy of a plane unit area of the solid will increase. This will reduce the apparent receding contact angle. Thus, in most cases, the apparent advancing angle is too high, and the apparent receding angle is too low. Furthermore, in the case of water, one would expect a solid which had been exposed to a humid atmosphere to yield a lower contact angle than a solid which had been kept dry. This would be due to an adsorbed film of water. Thus, it is not sufficient to measure contact angles at a constant relative humidity and temperature. One must control the time of exposure, and assume that the rate of water adsorption is the same for all solids studied.

Since the contact angle of a drop of liquid on a solid surface is directly influenced by the surface tension of the liquid, it is important that the liquid be uncontaminated by a surface-active material.

Molecular orientations at the surface greatly influence contact angles. Many molecules contain both hydrophobic and hydrophilic groups. Excellent examples of this are the fatty or resin acids. If the surface contains many carboxyl groups, the contact angle with water will be low. If, on the other hand, the carboxyl groups are buried in the solid, and remain there, the water will exhibit a stable high contact angle.

When either a mono- or a multi-molecular film of fatty or resin acids is cast onto a glass slide, the majority of the carboxyl groups will be oriented inward, since that insures the lowest free surface

energy. When water comes in contact with such an oriented surface, the natural tendency is for the carboxyl groups to reorient themselves so that they will be as close to the water as possible. This is a result of the strong polar or van der Waals forces existing between the carboxyl groups and water. Langmuir (49) called attention to this phenomenon when he showed that the contact angle of a monolayer of a fatty acid with a drop of water varied from 18 to 86°, depending upon the substrate on which the monolayer was deposited. Rideal (50) showed that such differences in the contact angles resulted from the differences in the attraction or strength of anchorage between the carboxyl end of the fatty acid and the solid substrate. Studies at The Institute of Paper Chemistry (51) have indicated that anchorage of size precipitates on cellulose fibers may be an important factor in the sizing of paper.

EXPERIMENTAL RESULTS

Cellulose surfaces, by virtue of their high free surface energies, are wet by water, and form near zero contact angles with it. This, of course, gives rise to rapid penetration of water through a sheet of cellulosic fibers. If, however, the surface of the cellulose can be modified by depositing on it materials which have low free surface energies, the net free surface energy of the fibers will be reduced, the work of adhesion will be decreased, and the contact angle will rise. If enough such material can be properly deposited and retained by the fibers, a sheet of paper or board can be made which will resist water penetration and that sheet is said to be sized. It is evident, therefore, that a prime requisite of any sizing agent is that it have a low free surface

energy, or in other words, that it form a high contact angle with water. The size precipitates prepared in this thesis have been investigated in that respect. Table XI lists the results of contact angle measurements of small droplets of water on films of the size precipitates.

TABLE XI

CONTACT ANGLES OF WATER DROPLETS ON FILMS OF SIZE PRECIPITATES

Initial [Ab]/[Al]	pH of Pptn.	θ_5[a], degrees	δ[b]	θ_{30}[a], degrees
Pure HAb	-	70.3	0.81	64.9
2.0	7.5	90.3	2.16	86.9
	6.5	92.6	0.64	88.7
	5.5	91.4	1.33	87.2
1.0	7.5	93.0	1.17	89.1
	6.5	94.3	1.49	85.6
	5.5	94.5	0.87	92.3
0.5	7.5	92.1	2.46	91.7
	6.5	90.8	4.39	86.6

[a] Subscripts on θ indicate the number of seconds of contact time tetween the water and the substrate before the measurement was taken. The data reported above are the average of at least four measurements of θ_5 and of at least two measurements of θ_{30}.

[b] Standard deviation among replicate measurements of θ_5.

Of those precipitates which were not entirely soluble in chloroform, only two were subjected to contact angle measurements. The standard deviation was much higher for these samples than for the others. Because of the low chloroform solubilities of the precipitates with abietate-to-

aluminum ratios of 0.5 and 0.2, it was difficult to cast a smooth film from them. In fact, a dried powder resulted when the normal slide casting technique was employed. This caused a loss of precision, and made the significance of the measurements doubtful. Consequently, contact angle measurements on other chloroform-insoluble precipitates were discontinued.

DISCUSSION

The photographic technique used to measure the contact angles provided good precision, as shown by the values for the standard deviation. Figure 6 is a typical photograph from which the contact angles were calculated.

It is believed that the method used in this thesis to coat slides produced smooth films. No surface roughness could be perceived when the coated slide was viewed in white light at the grazing angle. A further indication that the surfaces were smooth was the fact that when a water droplet was placed on a coated slide, the periphery of each water droplet was smooth and not ragged.

An analysis of variance of the data showed that samples with the same abietate-to-aluminum ratio yielded contact angles which were from the same statistical Universe. This analysis, which excluded the data from precipitates with an abietate-to-aluminum ratio of 0.5, also showed that there is a significant difference in the contact angles on films of different compositions. The latter result is consistent with Equation (17).

The data of Table XI indicate that the highest contact angle can be obtained by a film having an over-all abietate-to-aluminum ratio of 1.0. The low contact angle formed by water and abietic acid is probably due to some molecular orientation of the acid. Apparently, an appreciable amount of aluminum must be in the film to properly anchor and olate the abietate molecules and thus prevent them from exposing their carboxyl groups at the solid-liquid interface.

The change of contact angle with time was small but significant. This change was probably due in part to surface oxidation and hydrolysis, but mostly to molecular reorientation.

All of the size precipitates with the exception of pure abietic acid appear to have very low free surface energies and are capable of producing high and relatively stable contact angles with water. On this basis, one would predict that all of these precipitates should be able to size a sheet of paper or board. Before these precipitates can exert their sizing influence upon cellulose fibers, they must be uniformly and densely deposited upon the sized fibers so that the net free surface energy of the sized fibers is effectively lowered. This aspect of the sizing process will be discussed in the following section.

ELECTROPHORETIC MOBILITIES OF SIZE PRECIPITATE PARTICLES

THE THEORY OF ELECTROKINETICS

Ordinarily, when a solid is immersed in a liquid, an electrical double layer forms about the solid. Consequently, the solid phase assumes an electrical charge, and the liquid phase assumes an equal and opposite charge. The electrical double layer is a result of either (1) selective adsorption of ions in the case of ionizable liquids, or (2) molecular dipole orientations in the case of nonionizable liquids, or (3) ionization of surface molecules.

Thus, when colloidal particles are suspended in water, they will assume a certain electrical charge. If an electrical field of constant polarity is imposed upon this system, the particles will travel to one of the field poles, depending on the sign of their charge. This motion is commonly called "electrokinetic" motion. The rate of relative motion of the solid and liquid phases is proportional to the intensity of the applied field; it also depends upon the properties of the fluid, and on the structure of the electrical double layer, particularly on the zeta or electrokinetic potential as hereafter defined.

Figure 7 is an idealized visualization of the double layer which exists about solid particles immersed in an ionizable liquid such as water.

The double layer consists of two shells of ions of opposite charge. The inner shell is compact and narrow, but the outer shell is considered to be diffuse and wide with a high concentration of ions near the inner shell and a progressively lower concentration of ions as the distance from the surface of the particle increases. This double layer may be up to 10^3 Ångstroms thick (52). The inner shell adheres tightly to the solid,

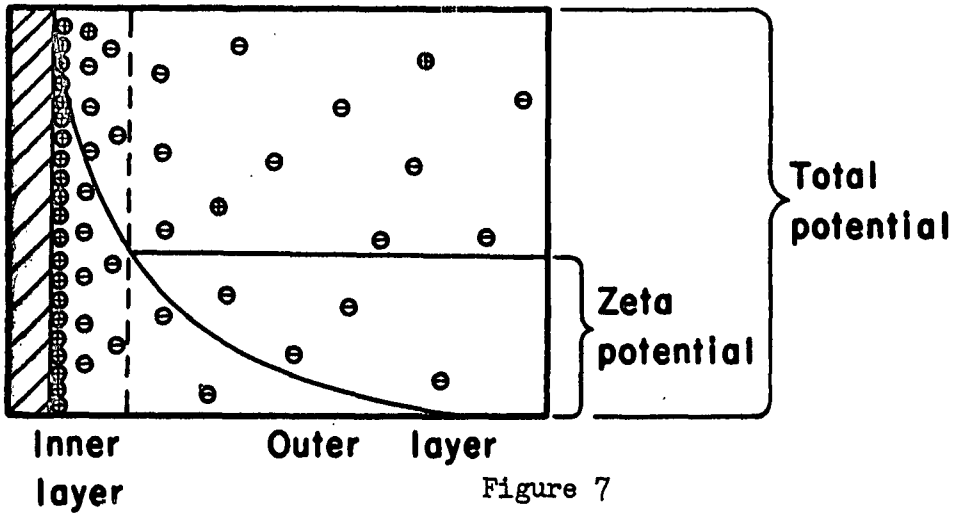


Figure 7

The Structure of the Double Layer
About a Suspended Solid Particle

and resists being stripped off when the particle is moved relative to the surrounding fluid. The outer shell, on the other hand, is free to remain with the fluid mass, and is thus capable of being severed from the solid particle. Thus, when the particle is moved relative to the fluid, a plane of shear exists in the double layer. This plane is represented by the dotted line in Figure 7.

The total potential drop between the surface of the colloidal particle and the bulk of the fluid may be divided into two parts, the first of which is the potential between the inner shell and the solid surface. The second part, which is the zeta or electrokinetic potential, is the potential drop through the outer shell. In other words, the electrokinetic potential is the potential existing between the plane of shear in the double layer and the bulk fluid when

the solid particles are moved relative to the fluid in which they are immersed. Adam (53) points out the fact that there is no intrinsic difference between electrokinetic motion and the motion of any charged particle, such as an ion in solution, in an electric field.

Debye and Hűckel derived a relationship between the zeta or electrokinetic potential and electrophoretic velocity. Their equation, according to Adam (53) is

$$\bar{v} = \zeta DX/6\pi\eta \qquad (30)$$

where

$\bar{v}$ = the average electrophoretic velocity of the migrating particles;

ζ = the electrokinetic potential of the particles;

D = the dielectric constant of the fluid phase;

η = the viscosity of the fluid phase; and

X = the potential gradient acting upon the particles.

Almost all workers in this field agree on the general form of Equation (30), but there is some disagreement with regard to the constant. Smoluchowski, by neglecting the effect of particle size and shape, arrived at the value of 4π. Because of this disagreement as the value of the constant, absolute values of the electrokinetic potential calculated from Equation (30) are doubtful. For this reason, some authors prefer to report relative values of the potential as expressed by the average electrophoretic mobility, $\bar{u}$. The mobility is defined as the electrophoretic velocity divided by the potential gradient of the field which is causing the particles to move. Referring to Equation (30),

$$\bar{u} = \bar{v}/X = \zeta D/6\pi\eta \qquad (31)$$

It is assumed that the dielectric constant and viscosity of the liquid phase remain constant for a given liquid at constant temperature. Then, Equation (31) simplifies to

$$\bar{u} = K\zeta \qquad (32)$$

Detailed discussions of electrokinetics have been written or compiled by Butler (54), Abramson (23), and Verwey and Overbeek (55).

APPLICATION OF ELECTROKINETICS TO THE SIZING PROCESS

Many authors have attributed the stability of colloidal dispersions to the electrokinetic potentials of the dispersed particles (25, 53). Briefly, the stabilization mechanism may be visualized as follows. When two particles approach each other closely enough, the van der Waals attractive forces cause them to adhere to each other. If the particles are similarly charged, work has to be done in bringing up one through the electrostatic repulsion of the other. The charge on the particles, acting through the electrokinetic potential which is produced in the surrounding fluid, hinders the approach of the particles to the critical distance at which they can adhere to each other. Conversely, if the particles possess opposite electrokinetic potentials, they are attracted to each other.

In the sizing process, there exists a situation where two different types of particles are suspended in the same fluid medium. One is the size precipitate, and the other is the cellulose fiber, both of which are

suspended in water which contains dissolved ions. As was indicated on page 64 of this thesis, both of these particles will assume certain electrokinetic potentials, as a consequence of the electrical double layer about them.

Gorham, Thode and co-workers, and Atwood (22, 19, 56) have investigated the electrokinetic properties of the alum-rosin size precipitates. They have suggested that the electrokinetic potentials of size precipitates and cellulose fibers are important factors in attracting the size precipitates to the fibers. These workers showed conclusively that the electrokinetic potential of the precipitate particles changes from negative to positive as the alum-to-rosin ratio is increased. When the alum-to-rosin ratio was plotted against the electrokinetic potential, the resultant curve was S-shaped.

Thode and Htoo (57) and Ninck Blok (13) have investigated the electrokinetic properties of cellulose fibers. The former determined the electrokinetic potential by the technique of the streaming current, whereas the latter employed the technique of electroosmosis. Both investigations showed that the cellulose fibers have a high negative electrokinetic potential when dispersed in pure water and that alum had to be added to a pH of 4.8 before the isoelectric point was reached.

Thode and co-workers (12) found a close correlation between sizing ability as measured by the ink penetration test and the electrokinetic potential of the size precipitate particles. They found that the most

rapid increase in sizing efficiency was accompanied by the most rapid increase in the electrokinetic potential.

The fact that abietic acid, a weak electrolyte, is a part of the size precipitate does not invalidate the application of electrokinetic principles to the sizing process since one of the causes of the electrokinetic potential may be ionization of surface molecules.

EXPERIMENTAL RESULTS

The use of sodium aluminate and perchloric acid made it possible to separate the effects of the aluminum and hydronium ions on the electrophoretic mobility of size precipitate particles. The use of these chemicals has also virtually eliminated anionic interference, such as is caused by the sulfate ion if alum is used. Figure 8 shows the effect of pH and initial abietate to aluminum mole ratio on the electrophoretic mobility. Figure 9 shows the effect of pH and foreign anions on the electrophoretic mobility of size precipitate particles. The data used to construct these curves may be found in Appendix II, Tables H and I.

DISCUSSION

The results are consistent with present theory and past observations of other systems, (12, 22, 56, 58). As was expected, the hydronium and hydroxyl ions most strongly influenced the potential, or mobility, of the size precipitate particles. Also, as the aluminum content of the precipitate increased, the effect of pH on the electrophoretic mobility decreased. In fact, those precipitates with an initial abietate-to-aluminum

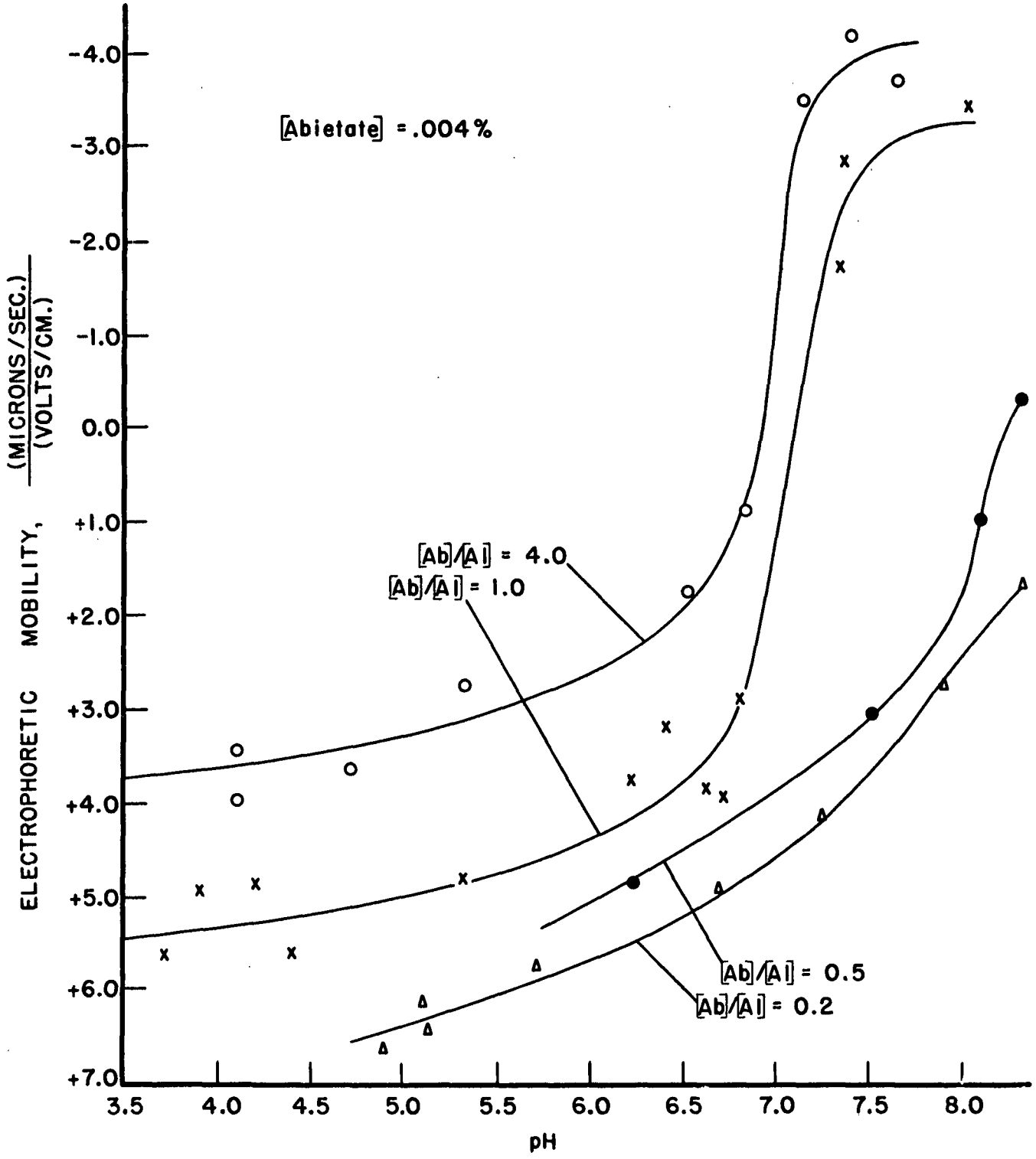


Figure 8. The Effect of pH and Initial Abietate to Aluminum Mole Ratio on the Electrophoretic Mobility of Aluminate-Abietate Precipitates

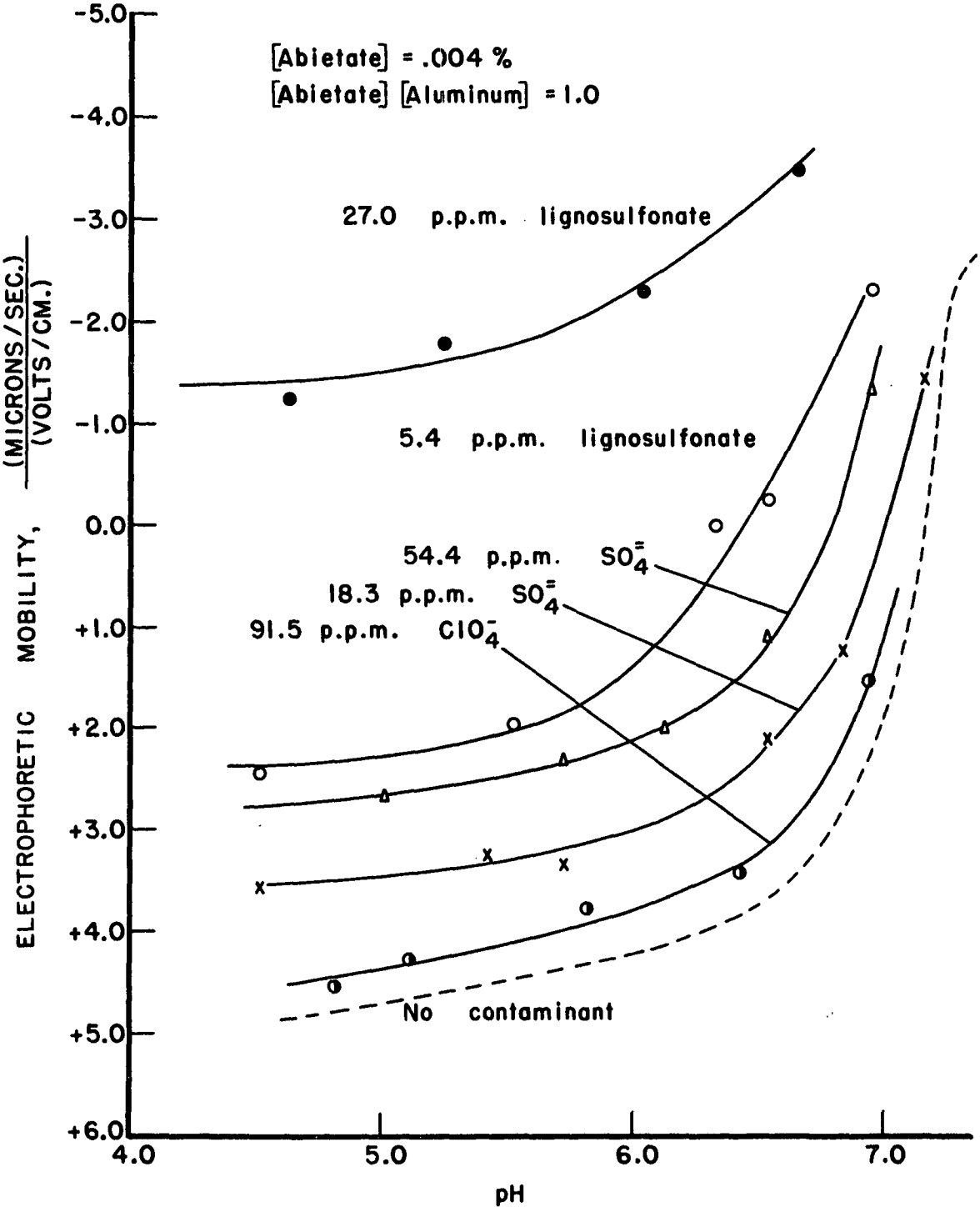


Figure 9. The Effect of Anions on the Electrophoretic Mobility of the Aluminate-Abietate Precipitates

mole ratio of 0.2 maintained a positive potential throughout the pH range of 4.9 to 8.2. This is in accord with the findings of Thode, Gorham, and Atwood (56), who studied the effects of soluble cations on the electrophoretic mobility of alum-rosin size precipitate particles. They found that only 50 p.p.m. of magnesium chloride in the suspension increased the mobility by 50% in the positive direction.

Figure 9 is evidence of the effect of foreign anions on the electrophoretic mobility. As was expected because of its very low sorbing and coordinating tendencies, the perchlorate ion was virtually ineffective in altering the mobility. On the other hand, only a small amount of a highly electronegative ion such as lignosulfonate was needed to markedly change the mobility. The fact that the sulfate ion lowered the electrophoretic mobilities of size precipitate particles is important because this ion is an unavoidable contaminant when alum is used.

The electrostatic theory of sizing postulates that the size precipitates are attracted to the fibers by virtue of the relative electrokinetic potentials of the size precipitate particles and the fibers. This theory has been described recently by Thode and co-workers (12). In this thesis, the electrostatic theory of sizing has been extended by postulating that the relative electrokinetic potentials of the precipitate particles and the fibers may also be an important factor in the mechanism of size retention. The phenomenon of size retention may be

treated as a special case of sol coalescence, the coalescence in this case occurring between the size precipitate particles and the cellulose surface. The electrokinetic potentials determine whether the precipitate particles and the fibers can approach each other closely enough for strong but short range attractive forces to exert their influence. These forces may be in the form of van der Waal's forces or hydrogen bonds.

Table XII shows the relationship between the size precipitate composition and the pH at which the particles will have an electrophoretic mobility of + 2.0.

TABLE XII

THE EFFECT OF COMPOSITION ON ELECTROPHORETIC MOBILITY OF SIZE PRECIPITATE PARTICLES

[Ab]/[Al] in the Ppt.	pH of Pptn. Necessary for $\underline{u}$ = + 2.0
4.0	6.5
1.0	6.9
0.5	7.9
0.2	8.2

Table XII suggests that if one wants to operate at an increased pH, and maintain the same degree of sizing, he must decrease the rosin-to-aluminum ratio in the size precipitate. This ratio, as shown in Table VI, page 44, is nearly the same as the initial rosin-to-aluminum mole ratio.

The effect of foreign anions on the electrokinetic potential may have a very important practical significance. The sulfate ion is

present in any water which has been treated with alum. In many closed white water systems, the sulfate ion concentration builds up to a very high value. By the same token, the lignosulfonate ion or other lignin residues may be present in appreciable concentrations, especially if the pulp is incompletely washed. The effect of these anions on the electrophoretic mobility can be seen in Figure 9. These data show that the presence of certain anions in the process water greatly affects the pH at which a given mobility or potential can be reached. Table XIII shows the pH at which a size precipitate with an abietate-to-aluminum ratio of 1.0 must be precipitated in anion-contaminated process water, if an electrophoretic mobility of +2.0 is to be maintained.

TABLE XIII

THE EFFECT OF ANIONS ON THE ELECTROPHORETIC MOBILITY OF SIZE PRECIPITATE PARTICLES

Contaminant	Contaminant Concentration, p.p.m.	Contaminant Concentration, molar	pH of Pptn. Necessary For $\bar{u}$ = +2.0
None	-	-	6.9
ClO_4^-	91.5	9.3×10^{-4}	6.8
$SO_4^=$	18.3	1.9×10^{-4}	6.6
$SO_4^=$	54.4	5.7×10^{-4}	6.1
Lignosulfonate	5.4	0.2×10^{-4}	5.5

Thus, if sizing is to be successfully carried out at near neutral pH values, anion contamination should be kept at a minimum. The anions undoubtedly fall in a series similar to the Hofmeister series (59) in their ability to affect the electrokinetic potential.

The sizing implications discussed above are strengthened by published observations of other workers. Chêne (15) reports being able to make well-sized handsheets from rosin, sodium aluminate, and alum. In order to get this sizing effect at pH values around 7.0, he had to use a rosin-to-aluminum ratio of 0.2. Barr (14) also showed that, operating at a pH of 5.5 and with the use of sodium aluminate, sizing results could be obtained which were comparable to those obtained with alum and rosin alone at a pH of 4.0. Simionescu (17), Dohne and Libby (16), and Wilson (10) all report similar observations. In all of these studies, the authors showed that the use of sodium aluminate accomplished two things: (1) a reduction in the rosin-to-aluminum ratio, and (2) a reduction in the sulfate ion concentration. These two factors both tend to make the electrokinetic potential of the size precipitate particles more positive and thus presumably tend to increase the size retention on the fibers. Stated in another way, these two factors allow the size precipitate particles to attain a given potential, and a given retention, at a higher pH.

Size precipitates which possess both low free surface energies and substantially positive electrokinetic potentials have been prepared. Theoretically, all of these precipitates should be capable of sizing a sheet of cellulose fibers. The ability of these precipitates to prevent water penetration was determined in the sizing studies which are described in the next section.

SIZING ABILITY OF SIZE PRECIPITATES UPON WOOD CELLULOSE FIBERS

EXPERIMENTAL RESULTS

Pulp was treated with preformed size precipitates and handsheets were made according to the procedures described earlier in this thesis. Table XIV gives the results obtained from size tests conducted on these handsheets.

TABLE XIV

SIZING STUDY A

Initial [Ab]/[Al]	pH of Pptn. and Sizing	Size[a] Time, sec.
0.75	7.5	0
	7.0	0
	6.5	0
	6.0	0
	5.5	4
0.50	7.5	0
	7.0	0
	6.5	2
	6.0	6
	5.5	22
0.32	7.5	18
	7.0	21
	6.5	35
	6.0	29
	5.5	33
0.20	7.5	13
	7.0	17
	6.5	34
	6.0	38
	5.5	37

[a] Size time expressed in seconds as determined by the fluorescence size test. Two separate batches of pulp were sized at each abietate-to-aluminum ratio and pH of precipitation. Two handsheets were made from each batch of sized pulp and duplicate size tests made on each handsheet. The size times reported above therefore are averages of eight separate determinations.

Table XV shows the different combinations of conditions tried in an attempt to size pulp at an abietate-to-aluminum ratio higher than 0.75. The same pH of precipitation and sizing, 5.5, was employed in all cases. Heating the sheets in a 110°C. oven for 30 seconds did not increase the size times.

TABLE XV

SIZING STUDY B

Initial [Ab]/[Al]	Ab, Based on Fiber, %	Pulp Consistency During Sizing, %	Size Time, sec.
5.0	3.0	0.70	0
3.0	5.0	0.78	0
2.0	3.0	0.10	0
2.0	6.0	0.14	3
2.0[a]	5.0	0.78	3
2.0[a]	4.0	0.10	15

[a] Precipitate formed and pulp sized in tap water.

When the fibers were treated with the size precipitate formed in the presence of the fibers, virtually no improvement over preformed sizing resulted.

DISCUSSION

It is concluded from the sizing results described above that the extracted pulp used in these experiments cannot be sized with less than 6% (based on pulp) of size precipitates which have abietate-to-aluminum ratios above 0.75 and which are formed in distilled water. Since it was shown earlier that these precipitates have very low free surface

energies, their inability to size the pulp may be caused by two other factors: (1) insufficient or nonuniform deposition of the size precipitate on the fibers, and (2) reorientation of the size precipitate carboxyl groups.

The size retention was determined on some of the handsheets. Two to three grams of the paper were placed in a Soxhlet extractor and extracted with 100 ml. of chloroform for five hours. The extract was concentrated, dried in a vacuum oven at 40°C., and weighed. The size retention was calculated by dividing the weight of the extracted size precipitate by the weight of the size precipitate added to the fibers during sizing. Table XVI gives the results of this study.

Those data are qualitative evidence that an increase in the electrokinetic potential of the size precipitate particles is accompanied by an increase in size precipitate retention. This evidence gives strength to the hypothesis presented on page 70, that the retention of size precipitate particles is influenced by electrokinetic potentials of the precipitate particles. The data of Table XVI show that all sheets which were sized at pH 5.5 retained enough size precipitate to impart at least some water resistance to the sheet, if the precipitate was uniformly deposited and anchored onto the cellulose fibers. Nevertheless, those sheets which were treated with precipitates in which the abietate-to-aluminum ratio was 2.0 were virtually unsized.

The fluorescence size testing apparatus is so constructed that the manner in which the water penetrates the sheet can be observed. The

TABLE XVI

RETENTION STUDIES

Initial [Ab]/[Al]	pH of Pptn. and Sizing	Ab During Sizing, Based on Fiber, %	Electrophoretic Mobility, μ	Size Ppt. Retained By Sheet, %	Size Time, sec.
2.0	7.5	3.0	-3.0	10	0
	6.5	3.0	+4.4	27	0
	5.5	6.0	+4.4	47	3
0.5	7.5	4.0	+3.2	9	0
	6.5	4.0	+4.4	13	2
	5.5	4.0	+5.5	35	22
0.2	7.5	4.0	+3.8	18	13
	6.5	4.0	+5.2	33	34
	5.5	4.0	+6.1	37	37

penetration was immediate and uniform in all of the sheets which exhibited zero or virtually zero size times. No pinholes and signs of irregular penetration were observed, indicating that the lack of sizing was not due to nonuniform deposition of the size precipitate. Since insufficient or irregular deposition of the size precipitate did not appear to be responsible for the lack of sizing in some of these sheets, it was deduced that the size precipitate carboxyl groups underwent reorientation upon contact with water.

When a size precipitate dries on a fiber surface, the precipitate molecules probably orient their carboxyl groups away from the air-size precipitate interface so that the interface will have the lowest free surface energy. The molecules located near this interface are blocked from the fibers and cannot be anchored to them. Yet, reorientation of

their carboxyl groups must be prevented if good sizing is to be maintained. It is proposed that the size precipitate molecules are immobilized by a mechanism of olation.

Earlier in this thesis, the mechanism of olation was discussed, and it was postulated that isolated size precipitates olate upon drying. If olation occurs during drying of the isolated size precipitates, then it must also occur during drying of the size precipitates on cellulose fibers.

The net effect of olation is to form strongly associated macromolecules. These macromolecules will be much more immobile by virtue of their size than the single molecules of aluminum abietates. This immobility of the size precipitate molecules will then retard reorientation of the hydrophilic groups toward the water-sized fiber interface, and good sizing will result.

It must be emphasized that effective olation is not limited to size precipitates in which the abietate-to-aluminum ratio is below 0.5. Effective olation occurs in precipitates in which there are sufficient amounts of aluminum hydroxide and aluminum monoabietate to form a large number of hydroxyl bonds. Under the conditions of precipitation employed in this thesis, such amounts were apparently reached when the initial abietate-to-aluminum mole ratios were 0.5 or less. Under different conditions which may include water purity and source of aluminum, this ratio would probably be different.

Based on experimental results obtained in this thesis, it is concluded that the size precipitate must contain both aluminum hydroxide and aluminum abietates in order to size a sheet of cellulose fibers.

Price (6, 7, 60) claimed that aluminum hydroxide was detrimental to sizing. Price's conclusions are disputable, however, since they were based only on the so-called "News Ink Test." This test measures the rate at which acidulated ink penetrates a sheet of paper or board. It cannot measure the true resistance of a sheet to water penetration because the acidulated ink undoubtedly differs from pure water in its effect on size precipitates.

Pulp which had been treated with size precipitates made in tap water produced handsheets which were moderately sized. On the other hand, pulp which had been treated with corresponding size precipitates made in deionized distilled water produced handsheets which were unsized, as shown in Table XIV and XV. Difficulty with sizing in distilled water has been observed by other workers, too. Jayme and Arledter (61) have studied the effect of water hardness upon sizing and have published the results shown in Table XVII.

These workers attribute the low sizing under conditions of high water hardness to the formation of calcium and magnesium resinates which, as shown by Back and Steenberg, (2) have a considerably higher free surface energy than aluminum rosinates. They do not explain why the lack of hardness in the process water also gave rise to poor sizing results. The following is a possible explanation.

TABLE XVII

THE EFFECT OF WATER HARDNESS UPON SIZING (61)

Hardness As $CaCO_3$, p.p.m.	Degree of Sizing[a] by the Jayme Method
0.0	.477
17.9	.533
35.8	.575
71.6	.567
107.2	.540
161.0	.490

[a] This is an ink adsorption method. The authors do not compare their "degree of sizing" with any of our known size tests, so one can only speculate that the minimum values represent poor sizing.

Most hard waters contain appreciable amounts of carbonate and bicarbonate ions. These ions are in the middle of the coordination range, so that they will have a significant tendency to coordinate with aluminum. In the alkaline solution, they will be in competition with the abietate ion for aluminum coordination sites. As the pH is lowered, the carbonate ion will convert to bicarbonate, which can also coordinate with the aluminum by replacing an abietate ion. As the pH is lowered further, the bicarbonate will be released as carbonic acid or carbon dioxide. The acid anion, in this case perchlorate, replaces the bicarbonate ion just as in a simple titration. At the same time, any uncoordinated abietate ions will precipitate as free abietic acid.

The perchlorate ion, however, has very little tendency to coordinate with aluminum. Thus, it is readily replaced by a hydroxyl ion,

which has a strong coordination tendency. The net effect of all this is that the precipitate will contain more hydroxyls in the form of aluminum monoabietate and aluminum hydroxide. The size precipitate will now have a greater tendency to olate, and better sizing will result.

GENERAL SUMMARY

SUMMARY OF EXPERIMENTAL RESULTS

Size precipitates were prepared by acidifying, with perchloric acid, dilute solutions of sodium abietate and sodium aluminate. These precipitates were prepared in four groups of different initial abietate-to-aluminum mole ratios (2.0 to 0.2), and each group contained precipitates which were precipitated or isolated at definite pH levels between 7.5 and 5.5. The following properties of these precipitates were studied:

1. Compositions,
2. Electrophoretic mobilities or relative electrokinetic potentials of precipitate particles,
3. Contact angles of water droplets on films of the precipitates, and
4. Sizing ability upon wood cellulose fibers.

The precipitates were isolated by centrifuging the suspension and drying the residue. The compositions of these isolated size precipitates were studied by means of organic solvent extractions and direct analyses for abietic acid, carbon and aluminum. From these analyses it was possible to ascribe empirical formulae to each of the isolated size precipitates. The following results were obtained from the composition studies.

1. The compositions of the isolated size precipitates formed from solutions of the same initial abietate-to-aluminum mole ratios were independent of the pH of precipitation or isolation.
2. The compositions of the isolated size precipitates were dependent upon the initial abietate-to-aluminum mole ratio.
3. Abietic acid was found in all precipitates.
4. None of the precipitates were found to be stoichiometric compounds, and thus were assumed to be coprecipitates of two or more compounds.
5. No evidence was found for the existence of a triabietate.
6. The isolated size precipitates possessed chloroform-benzene solubilities which indicated the presence of olation within the precipitates.

Films of isolated size precipitates were cast from chloroform solutions onto glass slides. The contact angles of water droplets on these films were determined by a photographic technique. The following results were obtained from this study.

1. Smooth films of precipitates with an over-all abietate-to-aluminum mole ratio of 1.0 formed average contact angles of 93.9°.
2. Smooth films of precipitates with an over-all abietate-to-aluminum mole ratio of 2.0 formed average contact angles of 91.4°.
3. Smooth films of pure abietic acid formed average contact angles of 70.3°.

4. Smooth films of precipitates with over-all abietate-to-aluminum mole ratios of 0.5 and less could not be cast, resulting in an inability to obtain precise contact angle measurements on these samples.

The relative electrokinetic potentials of the wet size precipitate particles were obtained by determining their electrophoretic mobilities. The mobilities were determined by an ultramicroscopic technique. The effects of certain anions on the mobility were also determined. The following results were obtained:

1. Both the pH of the suspension and the abietate-to-aluminum mole ratio of the precipitate influenced the electrophoretic mobilities.
2. When electrophoretic mobilities were plotted against the pH of the suspension, S-shaped curves resulted for those precipitates with abietate-to-aluminum mole ratios of 1.0 or more. A pronounced inflection occurred in the range of the isoelectric point (pH 6.5-7.0).
3. For precipitates with lower abietate-to-aluminum mole ratios, the curves tended to flatten out, until at an abietate-to-aluminum mole ratio of 0.2, the curve was almost linear.
4. As the pH of the suspension was increased, the electrophoretic mobility of the particles became more negative, for precipitates of constant abietate-to-aluminum mole ratios.
5. As the abietate-to-aluminum mole ratios of the precipitates were increased, the electrophoretic mobilities of the

particles became more negative, at constant suspension pH values.

6. Precipitates with an abietate-to-aluminum mole ratio of 0.2 failed to exhibit a negative electrokinetic potential, even at a pH of 8.2.

7. The effect of all the anions studied was to make the mobilities more negative. The magnitude of the effect was dependent upon the sorption tendencies and concentrations of the contaminant anions. A suspension of a precipitate with an initial abietate-to-aluminum mole ratio of 1.0 which was contaminated with 27 p.p.m. of sodium lignosulfonate failed to exhibit a positive electrophoretic mobility at any pH.

Cellulose fibers were treated with dilute suspensions of the size precipitates. Handsheets were made and tested for degree of sizing. The following results were obtained.

1. For size precipitates with the same initial abietate-to-aluminum mole ratio, the degree of sizing tended to increase as the pH of sizing decreased.

2. Fibers could not be satisfactorily sized at any pH with precipitates having an initial abietate-to-aluminum mole ratio of 0.75 or higher.

3. The best sized sheets were those which were treated with precipitates having an initial abietate-to-aluminum mole ratio of 0.2. This was the lowest ratio employed.

4. The amount of precipitate retained by the fibers increased as the pH of sizing decreased and as the initial abietate-to-aluminum mole ratio of the precipitate decreased.

A PROPOSED MECHANISM OF THE ALUMINATE-ABIETATE SIZING PROCESS

Any rosin sizing mechanism must consider at least three steps: (1) formation of potentially low free surface energy precipitates, (2) deposition of these precipitates onto the cellulose fibers, and (3) conversion of the wet size precipitate-fiber surface to a stable low free energy surface.

Based on the experimental results obtained in this thesis, a mechanism for the sodium abietate-sodium aluminate-perchloric acid sizing process is hereby proposed. The general principles should be applicable also to the commercial sodium rosinate-alum system.

FORMATION OF PRECIPITATES (Step 1)

An alkaline solution of sodium abietate and the aluminum ion contains several ionic species. These may include such ions as abietate, aluminate, and basic aluminum abietates. Upon the addition of acid, these ions begin to precipitate simultaneously as abietic acid, aluminum hydroxide, and aluminum abietates. Further addition of acid increases the amount of material precipitated, but does not change its composition. The composition of the coprecipitate is determined by the abietate-to-aluminum mole ratio existing in the solution at the instant of precipitation, and is independent of the pH of precipitation.

Coprecipitates rich in aluminum abietates are potentially good sizing agents, because these compounds exhibit a low free surface energy, when dried. Abietic acid has a higher free surface energy, and thus is not as good a sizing agent as the aluminum abietates. A favorable composition can be maintained by controlling the initial abietate-to-aluminum mole ratio.

DEPOSITION OF PRECIPITATES (Step 2)

The electrokinetic potentials of the size precipitate particles and cellulose fibers are the most important forces governing the deposition of the precipitates onto the fiber. When these two solid surfaces possess electrokinetic potentials which are opposite in sign, they are attracted to each other, and the size precipitate is deposited on the fibers. If, on the other hand, the sign of the potentials is the same, and the absolute values of the potentials are high enough to overcome thermal and mechanical agitation, the precipitate particles are repelled from the fiber surfaces, and little deposition occurs.

The pH of the sizing suspension and the presence of foreign ions greatly influence the electrokinetic potentials. Cellulose fibers exhibit a highly negative potential, the sign of which is difficult to reverse. Ionic contamination and pH greatly affect the potential of size precipitate particles and can reverse the sign of the potential. By controlling the ionic environment of the sizing suspension, size precipitate particles with high positive potentials can be produced. Factors which assure a high positive potential are (a) a low initial

abietate-to-aluminum mole ratio (0.5 or less), (b) a low pH of sizing (6.0 or less), and (c) a low concentration of easily sorbed anions in the sizing suspension.

CONVERSION INTO LOW FREE ENERGY SURFACES (Step 3)

Once the size precipitate is deposited on the fibers, the wet surface must be converted into one which will have a stable low free energy, giving rise to a system of effectively sized fibers. This conversion process occurs during the drying of the paper. Molecules of aluminum hydroxide, aluminum abietates, and cellulose hydroxyl groups associate by a mechanism called "olation." The olation immobilizes the individual precipitate molecules so that they are effectively bound to the cellulose fibers, and prevents the hydrophilic groups of the surface molecules from reorienting themselves to create a surface with a higher free energy.

The presence of aluminum hydroxide and aluminum monoabietate in the size precipitate is necessary for effective olation. This is accomplished by maintaining a low initial abietate-to-aluminum mole ratio. The absolute value of this ratio depends upon the system under consideration; in this case of the sodium abietate-sodium aluminate system, this value is less than 0.75%.

SUGGESTIONS FOR FURTHER WORK

1. A thorough investigation of the size-retention mechanism should be conducted. This investigation should take into account the effect of pH on the actual precipitate yields. The possibility of mechanical filtration should also be considered, taking into account the effect of precipitate particle size.
2. The occurrence and significance of aluminum hydroxide in size precipitates should be reaffirmed.
3. Difficulty with sizing in deionized distilled water was encountered in this thesis. Considerably better results were obtained when the sizing was done in tap water. The effect of water hardness on the composition of the size precipitate should be studied as one way of explaining these results.
4. The concept of olation was used in this thesis to interpret some of the experimental results. Proof should be sought for the occurrence of olation in size precipitates.

CONCLUSIONS

The following original conclusions are based on data obtained in a study of the sodium abietate-sodium aluminate-perchloric acid sizing system. These conclusions may also be applicable to the sodium abietate-alum sizing system.

1. Contrary to the conclusions of some authors who have studied the sodium abietate-alum sizing system, isolated size precipitates are not stoichiometric compounds.
2. Compositions of isolated size precipitates are independent of the pH of precipitation or isolation.
3. Compositions of isolated size precipitates are dependent upon the abietate-to-aluminum mole ratio initially existing in the alkaline solution.
4. Contrary to the conclusions of some authors who studied the sodium abietate-alum sizing system, aluminum triabietate is not a part of the size precipitate.

The following conclusions verified results obtained by other workers who studied the sodium abietate-alum system.

1. The electrophoretic mobility of size precipitate particles is dependent upon at least three factors: (a) composition of the precipitate, (b) pH of the suspension, and (c) the presence of other ions in the suspension.
2. Films of aluminum abietates exhibit a much lower free surface energy than do films of abietic acid, based on the contact angles of water on these films.

The following assumptions have been strengthened by evidence obtained in this thesis.

1. The retention of size precipitates on wood cellulose fibers is a strong function of the electrokinetic potential of the precipitate particles.
2. The size precipitates are coprecipitates of abietic acid, aluminum di- and monoabietate, and aluminum hydroxide.
3. In order to size wood cellulose fibers, the size precipitate must contain aluminum abietates and some aluminum hydroxide. Free abietic acid is not beneficial.
4. Coprecipitated aluminum hydroxide and aluminum abietates olate upon drying to yield a network of associated molecules.

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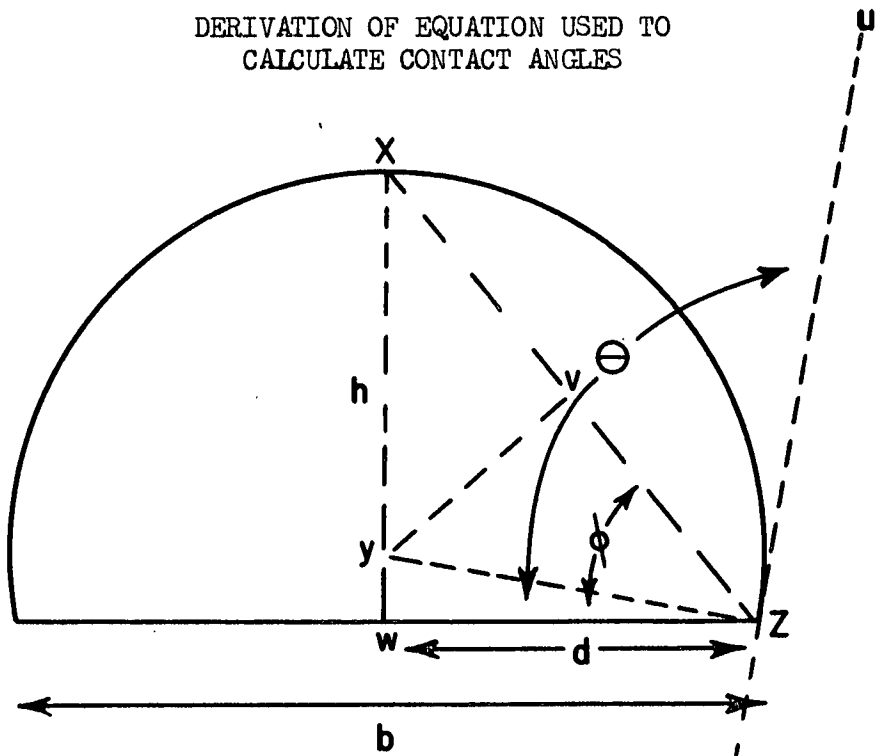
APPENDIX I

DERIVATION OF EQUATION USED TO CALCULATE CONTACT ANGLES



$$\tan \tfrac{1}{2}\Theta = 2h/b$$

The derivation of this equation is as follows:

(1) $\angle wyz + \angle yzw = 90°$

(2) $\angle xyz + \angle wyz = 180°$

therefore,

(3) $\angle xyz - \angle yzw = 90°$

(4) $\angle yzu = 90°$

therefore,

(5) $\angle xyz - \angle yzw = \angle yzu$

or,

(6) $\angle xyz = \angle yzu + \angle yzw = \theta$

(7) $\angle vyz + \angle vzy = 90°$

therefore, adding (1) and (7),

(8) $\angle vzy + \angle yzw + \angle vyz + \angle wyz = 180°$

(9) $\angle xyv + \angle vyz + \angle zyw = 180°$

therefore,

(10) $\angle yzw + \angle vzy = \angle xyv$

but,

(11) $\angle yzw + \angle vzy = \phi$

and,

(12) $\angle xyv = 1/2 \angle xyz = 1/2\theta$

therefore,

(13) $\phi = 1/2\theta$

(14) $\tan \phi = h/d = h/1/2b = 2h/b$

therefore,

(15) $\tan 1/2\theta = 2h/b$

APPENDIX II

TABLE A

SEPARATION OF SIZE PRECIPITATES INTO COMPONENTS

Initial[a] [Ab]/[Al]	pH of[b] Pptn.	Acetone Soluble, %	Acetone Insol. Fraction Sol. In 2:1 Chloroform-Benzene, %
2.0	7.5	21.6	100.0
	7.0	23.7	100.0
	6.5	22.4	100.0
	6.0	22.2	100.0
	5.5	24.2	100.0
1.0	7.5	10.9	100.0
	6.5	11.5	100.0
	5.5	13.5	100.0
0.5	7.5	7.9	42.5
	6.5	9.4	41.4
	5.5	8.6	41.0
0.2	7.5	0.4	0.5
	6.5	0.0	1.6
	5.5	0.5	1.2

[a] This is the mole ratio of abietate-to-aluminum ions existing in the alkaline solution prior to acidification and precipitation.

[b] pH of precipitation

TABLE B

ALUMINUM CONTENTS OF THE ACETONE EXTRACTS

Initial [Ab]/[Al]	pH of Pptn.	Extraction Time, hrs.	Al in Extract, %
1.0	6.5	0.7	0.12
2.0	6.5	0.7	0.43
2.0	6.5	39.0	0.30
3.0	5.5	0.7	0.17
4.0	5.5	24.0	0.20

TABLE C

EFFECT OF TIME ON ACETONE EXTRACTIONS

Initial [Ab]/[Al]	pH of Pptn.	Extraction Time, hrs.	HAb' in Size Ppt., %
1.0	6.5	0.7	13.7
1.0	6.5	18.0	11.9
2.0	6.5	0.7	23.6
2.0	6.5	18.0	22.5
2.0	6.5	39.0	25.3

TABLE D

ABIETIC ACID CONTENTS OF ISOLATED SIZE PRECIPITATES

Initial [Ab]/[Al]	pH of Pptn.	HAb[a] in Size Ppt., %
2.0	7.5	22.3
	7.0	21.9
	6.5	22.5
	6.0	20.2
	5.5	23.1
1.0	7.5	10.6
	6.5	11.9
	5.5	13.7
0.5	7.5	8.0
	6.5	9.0
	5.5	8.1
0.2	7.5	0.2
	6.5	0.2
	5.5	0.2

[a] Hab refers to abietic acid as determined by the sodium methoxide titrations. The values are based on unextracted isolated precipitates.

TABLE E

ANALYSES OF PRECIPITATE COMPONENTS

Initial [Ab]/[Al]	pH of Pptn.	Chloroform-Benzene Soluble Fraction Al, %	C, %	H, %	Chloroform-Benzene Insoluble Fraction Al, %	C, %	H, %
2.0	7.5	5.41	65.83	8.32	--	--	--
	7.0	5.28	67.69	8.51	--	--	--
	6.5	5.47	66.69	8.56	--	--	--
	6.0	5.30	69.79	9.01	--	--	--
	5.5	5.44	65.73	8.53	--	--	--
1.0	7.5	8.47	61.98	8.40	--	--	--
	6.5	8.27	62.40	8.53	--	--	--
	5.5	8.47	60.35	8.32	--	--	--
0.5	7.5	10.10	59.92	8.11	17.20	41.16	6.86
	6.5	10.00	59.68	8.09	17.10	41.34	6.78
	5.5	10.00	59.84	8.13	16.31	40.73	6.72
0.2	7.5	—	--	--	20.50	35.86	6.13
	6.5	—	--	--	20.90	35.13	6.15
	5.5	—	--	--	20.10	35.42	6.10

TABLE F

THE EFFECT OF COMPOSITION ON THE SINTERING AND MELTING RANGES OF SIZE PRECIPITATES

Initial [Ab]/[Al]	HAb, %	Sintering Range[b] °C.	Melting Range, °C.
1.0	11.9	200-210	348-360
1.0[a]	0.0	340-350	350-360
2.0	22.5	150-160	352-360
2.0[a]	0.0	330-340	340-355
4.0	63.0	110-125	300-310

[a] These precipitates have been acetone extracted, and presumably contain no free abietic acid.

[b] The sintering range is that range in which small fissures appear in the mass of sample powder, and in which the mass tends to shrink a little.

TABLE G

CONTACT ANGLES OF WATER DROPLETS ON FILMS OF SIZE PRECIPITATES

Initial [Ab]/[Al]	pH of Pptn.	θ_5[a], degrees	δ[b]	θ_{30}, degrees
Pure HAb	-	70.3	0.81	64.9
2.0	7.5	90.3	2.16	86.9
	6.5	92.6	0.64	88.7
	5.5	91.4	1.33	87.2
1.0	7.5	93.0	1.17	89.1
	6.5	94.3	1.49	85.6
	5.5	94.5	0.87	92.3
0.5	7.5	92.1	2.46	91.7
	6.5	90.8	4.39	86.6

[a] Subscripts on θ indicate the number of seconds of contact time between the water and the substrate before the measurement was taken. The data reported above are the average of at least four measurements of θ_5 and of at least two measurements of θ_{30}.

[b] Standard deviation among replicate measurements of θ_5.

TABLE H

THE EFFECT OF pH AND THE INITIAL ABIETATE-TO-ALUMINUM MOLE RATIO ON THE ELECTROPHORETIC MOBILITIES OF SIZE PRECIPITATE PARTICLES

Initial [Ab]/[Al]	pH of Pptn.	Av. Mobility of Particles, $\left(\frac{\text{microns/sec.}}{\text{volts/cm.}}\right)$
4.0	4.1	+3.40
	4.1	+3.94
	4.7	+3.59
	5.3	+2.71
	6.5	+1.70
	6.8	+0.81
	7.1	-3.56
	7.3	-4.23
	7.6	-3.74
1.0	3.7	+5.60
	3.9	+4.92
	4.2	+4.84
	4.4	+5.60
	5.3	+4.80
	6.2	+3.72
	6.5	+3.15
	6.6	+3.82
	6.7	+3.89
	6.8	+2.86
	7.3	-1.76
	7.3	-2.89
	8.0	-1.64
0.50	6.2	+5.00
	7.3	+3.17
	7.9	+0.78
	8.2	-0.76
0.20	4.9	+6.62
	5.1	+6.38
	5.1	+6.06
	4.7	+5.81
	6.7	+4.94
	7.3	+4.15
	7.9	+2.84
	8.2	+1.63

TABLE I

THE EFFECT OF FOREIGN ANIONS ON THE ELECTROPHORETIC MOBILITIES OF SIZE PRECIPITATE PARTICLES
(INITIAL [Ab]/[Al] = 1)

pH of Pptn.	Contaminant			Av. Mobility of Particles $\frac{\text{microns/sec.}}{\text{volts/cm.}}$
	Anion	P.P.M.	M.Eq./L.	
4.5	$SO_4^=$	18.3	0.38	+3.58
5.4				+3.25
5.7				+3.36
6.5				+2.10
6.6				+1.22
7.1				-1.48
5.0	$SO_4^=$	54.4	1.14	+2.66
5.7				+2.25
6.1				+1.97
6.5				+1.04
6.9				-1.37
4.8	$ClO_4^=$	91.5	0.93	+4.55
5.1				+4.30
5.8				+3.77
6.4				+3.42
6.9				+1.50
4.6	ligno-sulfonate[a]	27.0	0.086	-1.27
5.2				-1.83
6.0				-2.32
6.6				-3.56
4.5	ligno-sulfonate	5.4	0.017	+2.59
5.5				+1.98
6.3				0.00
6.5				-0.20
7.0				-2.33

[a] The sodium lignosulfonate used in these experiments was a sample of bleached salt prepared from Marathon OP. An equivalent weight of 340 was taken, based on its acid demand.

TABLE J

SIZING STUDIES

Initial [Ab]/[Al]	pH of Pptn.	Ab, Based On Fiber, %	Pulp Consistency During Sizing, %	Size[a] Time, sec.
5.0	5.5	3.0	0.70	0
3.0	5.5	5.0	0.78	0
2.0	5.5	3.0	0.10	0
2.0	5.5	6.0	0.14	3
2.0	5.5	5.0	0.78	3
2.0[b]	5.5	4.0	0.10	15
0.75	7.5	4.0	0.10	0
	7.0	4.0	0.10	0
	6.5	4.0	0.10	0
	6.0	4.0	0.10	0
	5.5	4.0	0.10	4
0.50	7.5	4.0	0.10	0
	7.0	4.0	0.10	0
	6.5	4.0	0.10	2
	6.0	4.0	0.10	6
	5.5	4.0	0.10	22
0.32	7.5	4.0	0.10	18
	7.0	4.0	0.10	21
	6.5	4.0	0.10	35
	6.0	4.0	0.10	29
	5.5	4.0	0.10	33
0.20	7.5	4.0	0.10	13
	7.0	4.0	0.10	17
	6.5	4.0	0.10	34
	6.0	4.0	0.10	38
	5.5	4.0	0.10	37
2.0[c]	5.5	3.0	0.19	4
2.0[c]	5.5	6.0	0.10	10
2.0[c]	5.5	4.1	1.40	3

[a] Size time expressed in seconds as determined by the fluorescence size test. Two separate batches of pulp were sized at each abietate-to-aluminum ratio and pH of precipitation. Two handsheets were made from each batch of sized pulp, and duplicate size tests were made on each handsheet. The size times reported above therefore are averages of eight separate determinations.

[b] The precipitate was formed and the pulp was sized in tap water.

[c] These size precipitates were formed in the presence of the pulp.

TABLE K

RETENTION STUDIES

Initial [Ab]/[Al]	pH of Pptn.	Ab, During Sizing, Based on Fiber, %	Size Ppt. Retained by Sheet, %
2.0	7.5	3.0	10.0
	6.5	3.0	27.7
	5.5	6.0	47.0
0.5	7.5	4.0	9.3
	6.5	4.0	13.8
	5.5	4.0	35.6
0.2	7.5	4.0	18.5
	6.5	4.0	33.6
	5.5	4.0	37.4